UNITED STATES DEPARTMENT OF COMMERCE
JESSE H. JONES, Secretary
NATIONAL BUREAU OF STANDARDS
Lyman J. Briggs, Director

✦

Journal of Research

of the

National Bureau of Standards

✦

Volume 32, Number 6
June 1944

[Published with approval of the Director of the Budget]

UNITED STATES
GOVERNMENT PRINTING OFFICE
WASHINGTON : 1944

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MATHEMATICAL TABLES

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U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1588

Part of Journal of Research of the National Bureau of Standards, Volume 32, June 1944

PURIFICATION OF SUBSTANCES BY SLOW FRACTIONAL FREEZING

Frank W. Schwab and Edward Wichers

ABSTRACT

This paper describes two technics for purifying substances by slow fractional freezing.

The first involves the slow lowering of a cylindrical cell, filled with the fused substance, through a heating coil in such a way that freezing begins at the bottom and progresses upward, as the cell emerges from the coil, until the whole mass has solidified. The solidified column, tube and all, is cut into the desired fractions.

The second technic, which is suitable for larger quantities, affords better control of the rate of freezing and provides a larger solid-liquid surface for a given quantity of material. A spherical flask filled with the liquid is cooled at a controlled rate in such a way that freezing begins at the wall of the flask and proceeds inward at a regulated slow rate until the desired fraction has solidified, after which the remaining liquid is siphoned out of the flask.

The purification of benzoic acid was much more rapid by this method than in earlier trials by crystallization from solvents. Acetanilide was also effectively purified. Observations incidental to the work show that the freezing point of pure acetanilide is 114.29 ±0.01° C.

In an earlier paper [1] brief reference was made to the use of fractional freezing as a means of purifying benzoic acid. This work was done on a very small scale. It followed closely a technic previously used by R. S. Jessup, of the Heat Measurements Section of this Bureau. A cylindrical tube, 2 cm in diameter, containing 50 g (45 to 50 ml) of the fused acid (mp 122.4° C) was slowly lowered through a heating coil. As the tube emerged from the coil, freezing began at the bottom and progressed until the whole mass was frozen. During the freezing, which extended over a period of 6 hours, the liquid portion was constantly stirred.

The foregoing procedure was also used to purify benzoic acid on a larger scale, for quantities of about 500 g. The glass tubes used were 4.6 cm in diameter, and the column of molten acid was about 30 cm long. The tube was lowered through the heating coil by supporting it on a platform floating in a tank of water, as shown in figure 1. Water was allowed to flow slowly from the tank through an outlet valve on a lower floor of the building. This was done to keep the hydraulic head substantially constant. Some difficulty was experienced with stoppage of the needle valve by particles of dirt. Alto-

[1] F. W. Schwab and E. Wichers, *Preparation of benzoic acid of high purity*, J. Research NBS 25, 747 (1940) RP1351.

gether, there were enough minor problems in operating this mechanically simple device to suggest that a somewhat more elaborate arrangement, such as a clock- or motor-driven movement, would have proved more satisfactory.

The liquid portion of the acid was stirred with a stream of nitrogen gas flowing from a Branham-Sperling bubbler.[2] The total period of

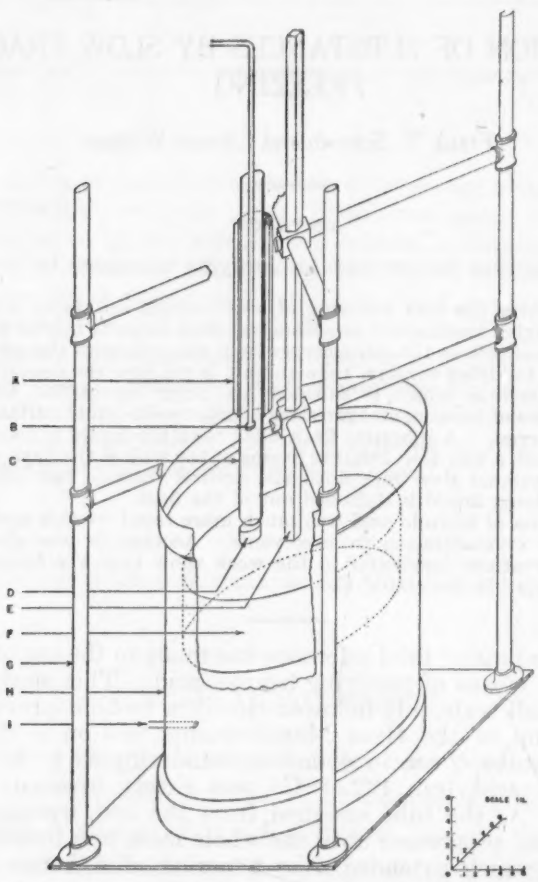

FIGURE 1.—*Sketch of apparatus for the purification of a substance by slow fractional freezing in a cylindrical cell*

A, Heating element backed by a layer of insulating material supported on an open Pyrex cylinder; B, a Branham-Sperling bubbler tip for stirring with nitrogen; C, cylindrical cell; D, cork support for cell; E, float guide; F, float; G, supports; H, container for water; and I, water outlet.

freezing was from 16 to 20 hours. An advantage of this method is that the acid is readily separated into fractions by allowing all of it to freeze and then cutting the column, tube and all, into suitable lengths.

A quantity of benzoic acid, which had an initial purity of 99.91 mole percent, was fractionally frozen three times in this apparatus, and each time the last one-fourth frozen was discarded. The yield of purified acid thus was about 40 percent. Its purity was 99.997 mole

[2] J. R. Branham and E. O. Sperling, *Bubbler tip of Pyrex glass for difficult absorptions*, J. Research NBS 22, 701 (1939) RP1214.

percent, as determined by measuring its freezing range in the manner described in an earlier publication.[3]

In the study of a process of this sort, it is helpful to know what fraction of the total impurity is removed by a single operation, in this case, a single crystallization. This fraction will be referred to as the efficiency of the process of purification. The over-all increase in purity can be used to calculate the efficiency of the process of purification. In this instance the substance contained, in 100,000 moles of starting material, 90 moles of impurities susceptible of removal by fractional freezing. After the third step of fractionation, the content of impurities was 3 moles in 100,000, or 3.3 percent of the amount originally present. Assuming equal efficiency of separation in all three steps of purification, the fraction of impurity not removed in a single step is the cube root of 0.033; that is, 0.32. The average efficiency of purification in this instance was therefore 68 percent.

When benzoic acid was fractionally frozen in the manner described, the solid material was clear and did not show evidence of entrapment of liquid or other macroscopic contamination. It seems probable that the relatively low efficiency of purification was caused by failure to maintain equilibrium at the solid-liquid interface. This could result from irregularities in the seemingly smooth progress of the cell through the heating coil, from irregular cooling caused by drafts or temperature changes around the apparatus, or simply from too rapid freezing. As freezing takes place the impurities increase in concentration in the very thin layer of liquid immediately adjacent to the solid surface. It is well known that this layer is not mixed with the body of the liquid by stirring, hence impurities can be transferred from it to the body of the liquid only by diffusion. It seems evident therefore that the degree of approach to ideal separation of impurities must be a function of the rate of deposition of crystalline material per unit area of surface.

Instead of attempting to improve the relative efficiency of purification by freezing in cylindrical cells, another apparatus was prepared in which the area of freezing surface was larger in relation to the quantity of material to be frozen, and the rate of freezing could be more steadily maintained and more easily regulated. In this apparatus it was possible also to handle much larger quantities than can well be done in cylindrical vessels. The apparatus is shown in figures 2 and 3. It consisted essentially of a long-necked, 5-liter flask of Pyrex glass imbedded in an especially effective thermal insulating material, silica aerogel, containing about 15 percent of silicon,[4] and provided with a small resistance heater wound around the base of the neck. The flask was filled with molten benzoic acid at a temperature about 10° C above its freezing point, enough to allow the loss of heat to the surroundings to become steady before freezing began. The liquid was agitated with a glass stirrer.[5] The stem of the stirrer passed through a hole in the flat bottom of a glass cylinder which closely fitted the neck of the flask, and which was placed with its

[3] F. W. Schwab and Edward Wichers, Precise Measurement of the Freezing Range as a Means of Determining the Purity of a Substance, Temperature—Its Measurement and Control in Science and Industry, p. 256–264 (Reinhold Publishing Corporation, New York, N. Y., 1941).
The impurities measured by the freezing range are limited to those soluble in the liquid but insoluble in the crystals. The same limitation applies, of course, to a process of purification based on fractional freezing.

[4] Ind. Eng. Chem. **31**, 827 (1939).

[5] The glass stirrer is made by sealing two rectangular flats about 1 cm by 6 cm to a glass rod. The long edges of the flats are centered and sealed to opposite sides of the rod, forming an angle at 20 to 25 degrees with it. A stirrer of this type vibrates less than the usual propeller type. The authors are indebted to W. G. Schlecht for the design of this stirrer.

bottom near the upper end of the resistance heater. The bottom of the sleeve formed a baffle to prevent loss of heat by convection in the neck of the flask and also sublimation of the acid into the neck. As the flask was imbedded in insulating material to a point above the heater on the neck, heat could be added to the system at this point to regulate to a limited extent the net loss of heat from the body of the flask. With the heater furnishing 5.8 watts, the rate of total loss

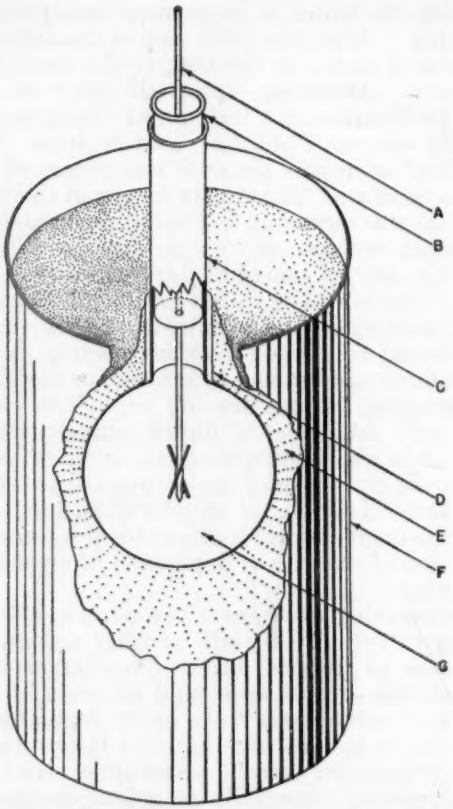

FIGURE 2.—*Apparatus for the purification of a substance by slow fractional freezing in a round-bottom flask.*

A, glass stirrer; B, sleeve to prevent loss of heat by convection; C, five-liter flask; D, heater for balancing the loss of heat through the neck of the flask; E, insulating material (silica aerogel); F, container for insulating material; and G, substance being purified.

of heat from the flask was about 7.5 watts, as determined from the amount of benzoic acid frozen and the latent heat of fusion. The rate of loss of heat was also roughly determined by the rate at which the liquid benzoic acid cooled just before it began to freeze.

After the desired fraction of the acid was frozen, the stirring assembly was removed and the remaining liquid was drawn off by suction. Then, a point-source radiant heater in the form of a small 45-watt lamp (automobile headlight type), with its electrical leads enclosed in a glass tube, was lowered through the neck to the center of the flask. Since benzoic acid is nearly opaque to red and infrared radiation, the heat from the lamp caused the surface layer of the acid

to melt. About 15 minutes' exposure to the lamp was required to melt 100 g. The surface of the solid which had been in contact with the impure mother liquor was thus washed by drawing off the remelted portion. This washing was done three times. The solid acid formed a nearly uniform layer about 2.8 cm thick over the whole inside of the flask except that it was thinner near the neck, where the level of the liquid had subsided because of the reduction in volume which occurred during freezing. The acid was nearly transparent except for shrinkage cracks which developed on cooling to room temperature.

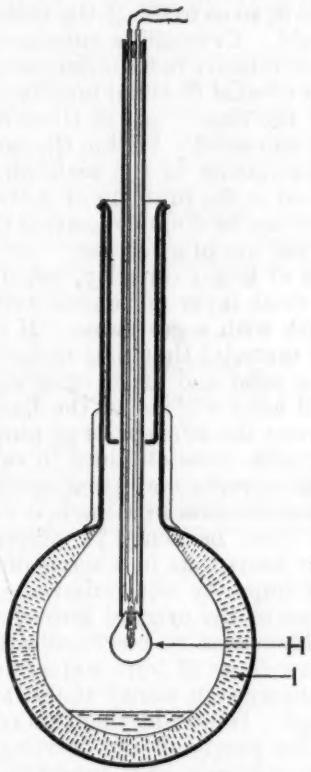

FIGURE 3.—*Assembly for partial melting and washing of crystallized material.*
H, Radiant heater; I, layer of crystals.

In the foregoing manner about 10 kg of benzoic acid was twice frozen, each time rejecting about 40 percent of the quantity in the flask. The combined products of the first fractionation of two 5-kg lots thus yielded more than enough to fill the flask for the second fractionation. The average purity of the product of the first fractionation was 99.986 mole percent and that of the second 99.998 mole percent. Since the starting material had a purity of 99.91 mole percent, it will be seen that the relative efficiency of separation was about 85 percent in each step. This figure is comparable with the efficiency of 68 percent reported for the cylindrical cell, because nearly the same fraction was rejected. It represents a marked gain in efficiency. This is attributable in part, perhaps, to a steadier rate of freezing, but

mainly to a slower rate of freezing. In the flask this was approximately 0.18 g/cm² of crystallizing surface per hour (a rate of growth of 0.024 mm per minute), whereas in the cylindrical cell it was 1.25 g/cm² of crystallizing surface per hour. It is obvious that, for any given quantity of liquid to be frozen, the use of the whole surface of a spherical container as a solid-liquid interface offers a marked advantage over freezing at one end surface in a cylindrical vessel. It is true that as freezing progresses in the flask the surface exposed to the liquid becomes smaller, thereby increasing the rate of freezing per unit area. However, the rate of loss of heat can be decreased to balance this change, or even to over balance it, so as to offset the increasing concentration of impurities in the liquid. Crystalline substances in general are such good conductors of heat relative to materials used for thermal insulation that the growing layer of solid does not greatly decrease the rate of loss of heat at the wall of the flask. All of these effects are decreased as the size of the flask is increased. Within the range of available sizes of flasks, the principal limitation to the scale on which this method of purification can be used is the problem of getting the frozen material out of the flask. This can be done by heating the whole flask in an air or liquid bath, or by the use of a solvent. An internal heater similar to that described, but of larger capacity, could also be used. In the present instance the thick layer of benzoic acid was melted by carefully warming the flask with a gas flame. If this is done, care must be taken to keep the material that first melts from freezing again in the space between the solid and glass, otherwise subsequent thermal expansion of the solid cake will break the flask.

A comparison between the efficiencies of purification here obtained by fractional freezing with those obtained in earlier work (footnote 1) on crystallization from solvents may be of interest. In that work the average efficiency of purification in a single crystallization from water was 14 percent and from benzene, 29 percent. These efficiencies were computed on the basis that in a series of n steps of purification the mean fraction of impurity not removed in a single step is the nth root of the fraction of the original impurity that remains after n steps. With these efficiencies 11 recrystallizations from benzene, in the manner there followed, or 25 from water, would have been needed to achieve the same increase in purity that was accomplished by the two fractional freezings. In considering this comparison it should be borne in mind that the purity of the starting material used in the recrystallization from solvents was considerably higher than that used for the fractional freezing and that the character of the impurities was not necessarily the same. It should also be noted that the efficiencies in question do not necessarily represent the highest that could be obtained by the respective methods.

The apparatus used for benzoic acid was also used (by W. H. Smith and W. W. Walton, of this Bureau) to purify a quantity of acetanilide. A single fractionation, in which about 50 percent was rejected, resulted in an increase in purity from 99.80 mole percent (determined from its freezing range) to 99.98 mole percent. The relative efficiency of purification therefore was 90 percent. In this instance the solid acetanilide was removed from the flask by dissolving it in hot benzene. On cooling the benzene solution the acetanilide was recovered in the desired form of small crystals. The indicated purity of the product therefore involved one step of crystallization

from benzene in addition to the fractional freezing. It was determined after removing the benzene trapped by the crystals. The extent of this incidental contamination by the solvent amounted to 0.11 percent for the crystals as dried at room temperature and 0.05 percent after the crystals were crushed somewhat. The amount of solvent in the substance was determined by a method, developed by the authors [6] for determining water and other volatile material in pure substances. The freezing temperature of this product, after removing benzene from it, was 114.28° C. The purity of the substance and the accuracy of the measurement of the temperature were sufficient to warrant giving 114.29° ± 0.01° C as the freezing temperature of pure acetanilide.

It is believed that slow fractional freezing deserves more consideration as a means of purification than it has received heretofore for substances stable at temperatures somewhat above their freezing points. The slow and steady rate of crystal growth that can be maintained offers a marked advantage over crystallization from solvents, as commonly practiced, with respect to approaching equilibrium between the solid and liquid phases. The method need not be limited to substances which freeze above room temperature. It should be equally applicable, with a suitable refrigerant, to substances which freeze at lower temperatures.

The authors express their appreciation to C. L. Gordon for the preparation of the drawings appearing in this paper.

WASHINGTON, April 1, 1944.

[6] A sample of acetanilide was fused in a glass apparatus, which was evacuated through a trap immersed in liquid air. The trap was then closed off from the rest of the apparatus, and the liquid air was removed, allowing the trap to warm up to room temperature. The amount of benzene removed from the acetanilide was estimated from the pressure, measured by means of a mercury manometer, and the temperature and volume of the closed system.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1589

Part of Journal of Research of the National Bureau of Standards, Volume 32, June 1944

A STUDY OF THE PROPERTIES OF HOUSEHOLD BLANKETS[1]

By Herbert F. Schiefer, Hazel Tharp Stevens,[2] Pauline Beery Mack,[3] and Paul M. Boyland

ABSTRACT

The fiber composition, weight, thickness, compressibility, compressional resilience, thermal transmission, air permeability, breaking strength, and shrinkage of 156 different blankets are recorded. The effects of laundering; of laundering and renapping; of laundering, renapping, and abrasion; of dry cleaning and renappng; and of dry cleaning, renapping, and abrasion on these properties of a large number of blankets are shown. A linear relationship was found between the compressional resilience and the wool content of cotton-wool blankets. The thermal transmission of the blankets was found to be independent of the kind of fiber. The reciprocal of thermal transmission was found to be related linearly to the thickness. The thermal transmission computed by means of the equation $1/T=3.0\ t_{0.1}+0.63$, where T is the thermal transmission in Btu/(°F hr ft²), and $t_{0.1}$ is the thickness in inches at a pressure of 0.10 lb/in.², was found to agree with the measured values within ±10 percent, 95 times out of 100. Empirical relationships were also found among thermal transmission, thickness at 1.0 lb/in.², and compressibility; and among thickness at 0.10 lb/in.², compressibility, and weight. The relation between breaking strength and weight, and that between breaking strength and compressibility, are discussed. Minimum requirements are suggested for the properties of blankets for use in a performance specification.

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[1] A part of this paper is based upon the data contained in the dissertation submitted by one of the authors in partial fulfillment of requirements for the Degree of Doctor of Philosophy at the Pennsylvania State College.

[2] Research Associate of the National Bureau of Standards, representing the Ellen H. Richards Institute, Pennsylvania State College, and Associate Professor of Textiles and Clothing, Colorado State College, Fort Collins, Colo.

[3] Director of Ellen Richards Institute and Professor of Textile Chemistry, Pennsylvania State College, State College, Pa.

I. INTRODUCTION

Blankets are an essential article in every home, hospital, and hotel, and in other places of abode. In time of war they form a vital part of the protective clothing of the soldier, sailor, and marine on battle fronts and in training camps. They furnish shelter to the wounded and to those forced to take to lifeboats and life rafts at sea. In time of peace blankets are an essential article for camping and other outdoor recreation and sport. In a major emergency they provide temporary shelter to the unfortunate victims.

Although blankets form such an essential part of life in war and in peace, adequate methods for testing them and essential information regarding their performance characteristics have not been available. New blankets are usually soft, lofty, fluffy, flexible, and warm. It is desirable to have them retain these characteristics during use. Changes in the characteristics of blankets during use are probably attributable mainly to the effect of laundering or dry cleaning. This is particularly true if the temperature and alkalinity of the water used in laundering wool or acetate blankets are too high or not controlled, or if the blankets receive excessive mechanical action during washing or dry cleaning.

New blankets differ considerably in their characteristics, and some will change more than others when washed or dry cleaned. A blanket which is considerably felted when new, for example, would not be expected to change greatly, whereas one which is soft, fluffy, and flexible is more likely to become felted and less flexible during cleaning. The cleaning procedure for blankets of the latter type would have to be controlled more closely to minimize changes in their desirable characteristics.

The results of tests on a large number of blankets of different fiber composition are given in this paper. The effects of laundering; of laundering and napping; of laundering, napping, and abrasion; of dry cleaning and napping; and of dry cleaning, napping, and abrasion on the properties of blankets are discussed. Information is given concerning the correlation between various properties of the blankets, and requirements for a performance specification of blankets are suggested.

II. MATERIALS TESTED

The blankets which were tested, 156 in number, are listed in table 1 according to their fiber composition and weight. Most of the blankets were obtained directly from manufacturers by the National Bureau of Standards, the Medical Corps of the United States Army, and the Ellen H. Richards Institute, Pennsylvania State College. Some were purchased from retail stores. A few were submitted for test by Government departments. It is believed that these blankets are a good representation of the qualities of blankets available at the time this investigation was made.

TABLE 1.—*Results of tests on 156 blankets*

Blanket No.	Fiber composition				Weight	Thickness at—		Compressibility	Compressional resilience	Thermal transmission	Air permeability at ½ in. H_2O pressure	Breaking strength (grab method)		Shrinkage in 10 washings [a]		Relative thermal insulation per unit weight [b]	Thermal insulating value [c]
	Wool	Cotton	Viscose rayon	Acetate rayon		0.10 lb/in.²	1.0 lb/in.²					Warp	Filling	Warp	Filling		
	%	%	%	%	oz/yd²	in.	in.	in./in. / lb/in.³	%	Btu/(°F hr ft²)	ft³/(min ft²)	lb	lb	%	%	°F hr ft² yd² / Btu oz / 150×10⁻³	%
1	100				5.6	0.080	0.044	0.34	49	1.15	257	32	19	10	3		28
2	100				8.4	.141	.083	.33	46			29	11				
3	100				8.5	.140	.089	.28	48			32	29				
4	100				8.6	.147	.091	.32	48			40	18				
5	100				9.5	.172	.099	.34	49	0.94	261	54	43	3	0	112	41
6	100				9.5	.182	.093	.42	52	.84	263	34	14	11	9	125	47
7	100				9.7	.167	.097	.31	43	.88	223					117	45
8	100				9.7	.161	.093	.32	44	.89	241					116	44
9	100				9.7	.198	.105	.43	47	.82	223	36	18			126	49
10	100				9.8	.164	.102	.30	45	.93	208	46	33	3	1	110	42
11	100				9.8	.193	.102	.40	50	.82	326	34	13	7	5	125	49
12	100				9.9	.178	.093	.40	47	.82	246					123	49
13	100				10.0	.164	.098	.33	45	.88	144					114	45
14	100				10.2	.137	.087	.28	36	.99	221	41	32	2	1	99	38
15	100				10.4	.192	.113	.35	45			24	12				
16	100				11.0	.184	.106	.39	48	.78	290	33	31	4	2	117	51
17	100				11.1	.185	.114	.31	55	.89	164	35	21	6	2	101	44
18	100				11.2	.188	.109	.36	45	.82	161	38	18			109	49
19	100				11.9	.191	.111	.36	48	.77	232	34	30	3	4	109	52
20	100				12.0		.108	.36	51	.69		45	21	*3	*5	121	57
21	100				12.0	.193	.103	.49	54	.75	111	50	21	3	10	111	53
22	100				12.1	.204	.119	.37	48	.78	264	30	22	3	3	106	51
23	100				12.1	.221	.137	.28	46			31	26				
24	100				12.5	.172	.105	.27	42	.86	152					93	46
25	100				12.5	.236	.139	.35	46			32	22				
26	100				12.6	.231	.122	.34	47	.74	498	37	39	12	0	107	54
27	100				12.6		.126	.34	44	.75		37	12	*7	*1	106	53
28	100				13.0	.249	.147	.33	42			40	52				
29	100				13.0	.214	.134	.30	44	.80	103					96	50
30	100				13.0	.228	.115	.43	39	.75	187	51	31	4	6	103	53

See footnotes at end of table.

TABLE 1.—*Results of tests on 156 blankets*—Continued

Blanket No.	Fiber composition				Weight	Thickness at—		Compressibility	Compressional resilience	Thermal transmission	Air permeability at ½ in. H_2O pressure	Breaking strength (grab method)		Skrinkage in 10 washings [a]		Relative thermal insulation per unit weight [b]	Thermal insulating value [a]
	Wool	Cotton	Viscose rayon	Acetate rayon		0.10 lb/in.²	1.0 lb/in.²					Warp	Filling	Warp	Filling		
	%	%	%	%	oz/yd²	in.	in.	in./in. / lb/in.²	%	Btu/(°F hr ft²)	ft³/(min ft²)	lb	lb	%	%	°F hr ft² yd² / Btu oz 75×10⁻³	%
1	100				13.1	.128	.083	.23	50	1.01	77	68	56	8	4		37
2	100				13.1	.215	.127	.32	44			48	14				
3	100				13.7		.138	.30	50	.74		45	41	*8	*6	99	54
34	100				13.8	.292	.164	.41	46	.69	263	43	33	7	3	105	57
35	100				13.8	.204	.120	.36	54	.73	190	40	25	6	3	99	54
36	100				14.3	.265	.167	.33	47	.73	153	46	35			96	54
37	100				14.3	.152	.098	.23	48	.96	101	63	59	8	6	73	40
38	100				14.5	.305	.161	.45	46	.72	280	30	24	11	12	96	55
39	100				14.6	.147	.098	.30	48	1.00	70	77	59	8	4	69	38
40	100				14.6	.253	.153	.31	44	.75	148					91	53
41	100				14.6	.136	.095	.21	53	.96	91					71	40
42	100				14.6	.200	.121	.28	45	.85	187					81	47
43	100				14.7	.233	.157	.28	50	.82	127	56	48	10	9	83	49
44	100				14.8	.165	.114	.23	44	.93	125	29	26	3	0	73	42
45	100				14.9	.270	.143	.46	51	.65	216	33	32	7	5	103	59
46	100				14.9	.230	.128	.37	50	.78	212	56	36	8	3	86	51
47	100				14.9	.137	.095	.21	49	.91	95					74	43
48	100				14.9	.242	.136	.34	46			81	50	[a]			
49	100				15.0	.231	.143	.31	41	.78	173					86	51
50	100				15.2	.250	.165	.27	44	.75	105					88	53
51	100				15.3	.212	.143	.24	48	.85	103	54	63	7	4	77	47
52	100				15.3	.178	.118	.29	35	.85		53	54			77	47
53	100				15.9	.178	.121	.23	50	.93	53	74	70	8	3	68	42
54	100				16.4	.141	.103	.18	49	.93	94					66	42
55	100				16.5	.151	.100	.22	48	.95	45	68	71	8	3	64	41
56	100				16.7	.193	.125	.31	40	.83		58	51			72	48
57	100				16.7	.156	.114	.19	51	.91	99					66	43
58	100				17.5	.256	.159	.32	52	.77	142	31	27	6	0	74	52
59	100				17.7	.277	.182	.28	48	.72	99	57	75			78	55
60	100				17.8	.207	.137	.24	42	.87	101	75	48	2	1	65	46
61	100				18.3	.170	.120	.23	41	.90		79	67			61	44
62	100				19.3	.175	.130	.24	39	.92							

61	100				18.3	.170	.120	.23	41	.90		79	67			61	44
62	100				19.3	.175	.120	.24	39	.93		73	72			56	42
63	100				19.4	.404	.221	.40	50	.57	122					90	64
64	100				22.4	.382	.228	.35	49	.60	86					74	63
65	80	20			8.8	.160	.089	.38	47			33	17				
66	71	29			9.3	.156	.085	.38	42	.91	116					118	43
67	80	20			9.6	.136	.087	.26	50	.97	124	46	46	8	12	107	39
68	75	25			10.0	.198	.097	.42	51		232	48	31				
69	73	27			10.1	.159	.087	.34	41	.94	187					105	41
70	75	25			10.5	.164	.095	.33	42	.93	105					102	42
71	79	21			11.4	.185	.106	.36	43	.82	160	46	42	2	**1	107	49
72	84	16			12.2	.243	.148	.38	44			37	22				
73	81	19			12.2	.122	.083	.20	38			22	11				
74	98	2			14.2	.138	.096	.22	42	.97	93	45	38	3	2	78	39
75	80	20			14.7	.269	.173	.29	39			49	60				
76	81	19			15.3	.205	.122	.30	42	.88	134					74	45
77	82	18			15.4	.292	.169	.41	41	.72	151					90	55
78	86	14			15.6	.145	.104	.19	42	.95	123	45	21	3	1	67	41
79	91	9			15.8	.139	.096	.20	41	1.00	126	59	39	3	1	63	38
80	87	13			19.7	.240	.159	.26	49	0.84	74	56	88	12	4	60	47
81	51	49			9.8	.194	.114	.37	36	.81	266	35	20	5	7	126	49
82	62	38			12.4	.145	.100	.21	36			24	19				
83	50	50			14.4	.170	.109	.27	37	.86	88	53	59	12	10	81	46
84	53	7			14.7	.155	.111	.22	36	.95	63	22	41	4	4	68	41
85	50	)			14.7	.179	.114	.27	35	.89	90	52	65	13	11	77	44
86	59	41			14.8	.167	.114	.21	40			38	24				
87	50	50			15.2	.175	.114	.25	35	.90	85	53	90	12	13	73	44
88	50	50			15.6	.168	.110	.25	36	.90	82	52	84	11	13	71	44
89	49	51			19.1	.203	.147	.18	32			36	34				
90	28	72			7.0	.143	.076	.37	34			28	15				
91	41	59			7.2	.123	.073	.30	42			32	9				
92	26	74			7.5	.143	.082	.35	31			45	5				
93	27	73			7.8	.149	.085	.38	33	.85		31	11			151	47
94	33	67			9.7	.122	.070	.29	31	1.06	115					97	34
95	26	74			9.9	.142	.089	.28	35			54	18				
96	37	63			9.9	.120	.071	.30	38	1.04	124	56	38	14	0	97	35
97	34	66			10.0	.135	.072	.32	36	0.97	107					103	39
98	25	75			10.9		.152	.44	33	.67		41	17	*7	*7	137	58
99	40	60			11.1	.147	.087	.29	39	.97	105	63	33	12	0	93	39
100	25	75			11.8	.239	.139	.36	29			39	35				

See footnotes at end of table.

TABLE 1.—*Results of tests on 156 blankets*—Continued

Blanket No.	Fiber composition				Weight	Thickness at—		Compressibility	Compressional resilience	Thermal transmission	Air permeability at ½ in. H_2O pressure	Breaking strength (grab method)		Shrinkage in 10 washings [a]		Relative thermal insulation per unit weight [b]	Thermal insulating value [c]
	Wool	Cotton	Viscose rayon	Acetate rayon		0.10 lb/in.²	1.0 lb/in.²					Warp	Filling	Warp	Filling		
	%	%	%	%	oz/yd²	in.	in.	in./in. lb/in.²	%	Btu/(°F hr ft²)	ft³/(min ft²)	lb	lb	%	%	°F hr ft² yd²/Btu oz	%
101	29	71			12.4	.266	.156	.37	31			42	34				
102	29	71			12.6	.123	.088	.17	38			28	26				
103	25	75			13.5	.215	.137	.30	27	.84	135	47	45	15	13	88×10^{-3}	47
104	25	75			13.6	.206	.128	.31	29	.80	137	58	47	16	12	92	50
105	25	75			14.2	.213	.135	.30	29	.85	116	58	62	12	10	83	47
106	25	75			14.2	.211	.131	.30	26	.80	135	62	53	16	14	88	50
107	38	62			15.1	.204	.117	.29	35	.86	102					77	46
108	38	62			15.1	.174	.113	.24	38	.96	86					69	40
109	3	97			6.8	.200	.097	.39	18	.92		31	10			160	42
110	4	96			6.9	.140	.080	.39	26	.93		35	13			156	42
111	6	94			6.9	.142	.084	.32	28			36	21				
112	1	99			7.6	.133	.084	.29	34			33	10				
113	17	83			8.2	.142	.084	.32	34			43	8				
114	1	99			8.7	.215	.118	.35	20	.87						132	46
115	3	97			8.9	.195	.118	.37	24	.86		34	14			131	46
116	8	92			9.4	.200	.113	.36	33			36	19				
117	5	95			10.6	.235	.128	.32	16	.90		28	37			105	44
118	2	98			11.1	.195	.132	.27	35			54	21				
119		100			4.1	.059	.031	.35	31	1.07		30	8			228	33
120		100			4.3	.065	.033	.39	28	1.05		29	12			221	34
121		100			4.6	.079	.039	.36	29			29	11				
122		100			4.8	.070	.039	.33	33	1.06						196	34
123		100			5.4	.097	.052	.50	24	0.98		31	19			189	39
124		100			6.0	.081	.046	.37	29	1.05		37	28			159	34
125		100			6.4	.103	.060	.37	28	1.03		27	31			152	36
126		100			6.5	.100	.058	.34	26	1.00		21	37			154	38
127		100			9.5	.182	.114	.38	29	0.84	178	41	13	7	**1	125	47
128		100			11.0	.192	.126	.32	29	.86	155	38	24	6	4	106	46
129	78		22		15.6	.208	.133	.31	33	.77		42	37			83	52
130	33	62	5		10.0	.179	.109	.34	33	.82		33	19			122	49
131	29	53	18		13.9	.231	.160	.33	32	.76	178	43	45	4	9	95	52

131	29	53	18		13.9	.231	.160	.33	32	.76	178	43	45	4	9	95	52
132	27	55	18		8.7	.141	.081	.36	33		208	47	23				
133	26	43	31		11.8	.204	.128	.37	33	.80	248	41	30	5	**2	106	50
134	25	38	37		12.4	.313	.175	.44	19	.70		42	35			115	56
135	24	37	39		12.3	.317	.172	.49	20	.68		40	32			120	57
136	23	38	39		11.1	.237	.126	.38	24	.81		42	30			111	49
137	23	24	53		11.7	.307	.149	.50	18	.71		36	35			120	56
138	23	31	46		13.0	.275	.172	.39	29	.73	224	41	32	4	1	105	54
139	21	47	22		10.7	.303	.129	.56	18	.68		34	23			138	57
140	17	55	28		6.6	.212	.074	.57	17	.84		30	14			180	47
141	12	1	87		12.8	.281	.175	.36	24	.74	216	33	40	5	7	106	54
142	7	55	38		8.6	.232	.095	.46	16	.83		36	22			140	48
143	6	62	32		12.2	.212	.145	.31	26	.82	168	45	32	4	4	100	49
144		25	75		10.0	.279	.126	.57	21	.73		38	19			137	54
145		18	82		13.9	.154	.112	.22	22	.91	74	57	57	9	**5	81	43
146		13	87		15.1	.239	.148	.35	25	.83	343	49	50	7	10	80	48
147	75			25	15.9	.144	.089	.29	40	.87		56	61			72	46
148	70			30	16.3	.143	.099	.23	53	.93	30					66	42
149	50			50	14.7	.110	.070	.27	30	.99		55	52			69	38
150	27	22		51	14.5	.245	.152	.31	30	.76	141	50	56	10	7	91	52
151	25	25		50	5.3	.076	.040	.33	33	1.04	269	31	16	6	1	182	35
152	25	26		49	10.6	.286	.153	.49	30	0.68	331	36	22	11	10	139	57
153	25	25		50	15.9	.229	.155	.30	29	.75		54	58			84	53
154	22	27		51	15.5	.253	.157	.33	29	.72	160	49	71	8	12	90	55
155				100	14.2		.124	.25	41	.78		55	8	*3	*2	90	51
156				100	19.6		.130	.23	43	.77		65	45	*5	*0	66	52

* The values marked with a single asterisk are shrinkage after 5 washings. The values marked with 2 asterisks indicate a stretch instead of a shrinkage.

[b] $\frac{1}{TW}$

[c] $\frac{100(1.60-T)}{1.60}$

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III. TESTING PROCEDURE

The weight, thickness, compressibility, compressional resilience, breaking strength, shrinkage, air permeability, and thermal transmission of the blankets before and after washing or dry cleaning were measured with equipment[4] and methods of testing[5] previously described.

Weight is expressed in ounces per square yard hereafter referred to as areal weight. Thickness is given for stated pressures. Breaking strength is expressed as the load at failure in the "grab" procedure, wherein a specimen considerably wider than the clamps is tested. Shrinkage is expressed as the percentage change in the dimensions of the specimen in each of its two principal directions.

Compressibility, $(\Delta t/t_{1.0})/\Delta P$, is the decrease in thickness, Δt, in unit thickness at a pressure of 1.0 lb/in.^{2}, $t_{1.0}$, per unit change of pressure, ΔP. For convenience in the numerical calculation of compressibility, Δt is taken to be $t_{0.5}-t_{1.5}$, where $t_{0.5}$ and $t_{1.5}$ are the thickness values at pressures of 0.5 and 1.5 lb/in.^{2}, respectively, and ΔP, the difference between these two pressures, is therefore 1.0 lb/in^2. The unabridged unit, (in./in.)/(lb/in.^{2}), rather than the contracted form, in.^{2}/lb, previously used, is used in this paper because its physical meaning is more readily understood.

Compressional resilience is the work recovered when the pressure is decreased from 2.0 to 0.10 lb/in.^{2} expressed as a percentage of the work done when the pressure is increased from 0.10 to 2.0 lb/in^2.

Thermal transmission is measured by the rate of loss of heat energy through a unit area of the material per unit temperature difference, when there is a temperature difference of 20°C (68°F) between the hot plate and the hood (cold plate).

Air permeability is measured by the volume of air flowing in unit time through a unit area of the material when the pressure difference across one thickness of the blanket is ½ in. of water.

The blankets were conditioned by exposure to air having a relative humidity of 65 percent and a temperature of 70°F, with a tolerance of ±2 percent in relative humidity and ±2°F in temperature. All the tests, except thermal transmission, were made under these conditions.

Some of the blankets were washed 10 times in a commercial laundry without brushing or renapping after washing. Some were washed 10 times in the United States Army laundry at Fort Myer, Va., without renapping after washing. Others were washed 10 times at the National Bureau of Standards in a reversing wash wheel, in an 0.5-percent soap solution at 100° F for 15 min, followed by three 5-min rinses also at 100° F. The samples were then centrifuged for 1 min and dried in a horizontal position without tension. Some of these blankets were not renapped after each washing, whereas others were renapped after each washing. Duplicate samples of the latter were renapped and then abraded before the next washing to simulate the mechanical wear during use. Some of the blankets were dry

[4] Herbert F. Schiefer, *The Compressometer, an instrument for evaluating the thickness, compressibility, and compressional resilience of textiles and similar materials*, BS J. Research **10**, 705 (1933) RP561.
R. S. Cleveland, *An improved apparatus for measuring the thermal transmission of textiles*, J. Research NBS **19**, 675 (1937) RP1055.
Herbert F. Schiefer and Paul M. Boyland, *Improved instrument for measuring the air permeability of fabrics*, J. Research NBS **28**, 637 (1942) RP1471.

[5] Herbert F. Schiefer, *Advantages of a blanket-and-sheet combination for outdoor use*, J. Research NBS **30**, 209 (1943) RP1529.

cleaned in a commercial plant with a washer 36 in. in diameter and 54 in. in length and normal load of 60 to 70 lb. Stoddard solvent, conforming to Commercial Standard Specification CS3–40, and a commercial paste type of soap, which contained about 10 percent of water, were used. One pound of soap was used for every 25 lb of load. The dry cleaning procedure consisted of a 10-min run in solvent without soap; a 20-min run in solvent and soap; and a 20-min rinse in solvent. The blankets were centrifuged and then dried in a tumbler for 30 min. The temperature of the air leaving the tumbler was approximately 160° F. The dry-cleaned samples of blankets were renapped after each dry cleaning. Duplicate samples were renapped and then abraded before the next dry cleaning.

The properties of the blankets were measured when new and most of them were measured again after 1, 5, and 10 washings or dry cleanings.

Some of the laundered and dry-cleaned blanket samples were abraded with a machine similar to the one developed by Haven.[6] The Haven machine was modified to permit testing a blanket sample 14 in. wide and 18 in. long. The length of the stroke was reduced to 14 in. The area abraded was 14 by 14 in. The blanket sample was fastened to two clamps specially constructed for these tests. One clamp was fastened to the reciprocating mechanism of the machine. The blanket sample was placed over a horizontal, smooth shaft, which was 1 in. in diameter and mounted in ball bearings, and to the other clamp was attached a 5-lb weight. A horizontal bar weighing 5 lb [7] and covered with No. 8 duck was placed on the blanket directly above the shaft. This bar was rectangular in cross section and was held in place by vertical guides at each end. The blanket sample was drawn back and forth over the shaft, which rotated freely, and underneath the duck-covered bar, which remained stationary. The back-and-forth movement of the blanket sample relative to the duck fabric abraded the nap of the blanket. After 200 back-and-forth movements, the blanket sample was turned over and the reverse side was abraded the same number of strokes. This abrasion procedure was repeated before each subsequent laundering or dry cleaning.

The fiber composition of the blankets was determined microscopically. If more than one kind of fiber was found in a blanket, a chemical analysis was made.

IV. RESULTS AND DISCUSSION

The results of the tests of the original blankets are given in table 1. The results of the tests of the blankets after laundering and dry cleaning are omitted to conserve space; however, the over-all changes in the properties of the blankets are brought out in the following discussion.

1. EFFECT OF LAUNDERING

The effect of laundering without renapping on the properties of 43 blankets is shown in figure 1, where the amount of change in a property after 1, 5, and 10 washings, expressed as a percentage of the value of the property of the blanket when new, is plotted as abscissa. For

[6] Textile World **76**, p. 2654–2656, 2662 (1929).
[7] In some of the early tests a weight of 1 lb was used but was found to be insufficient.

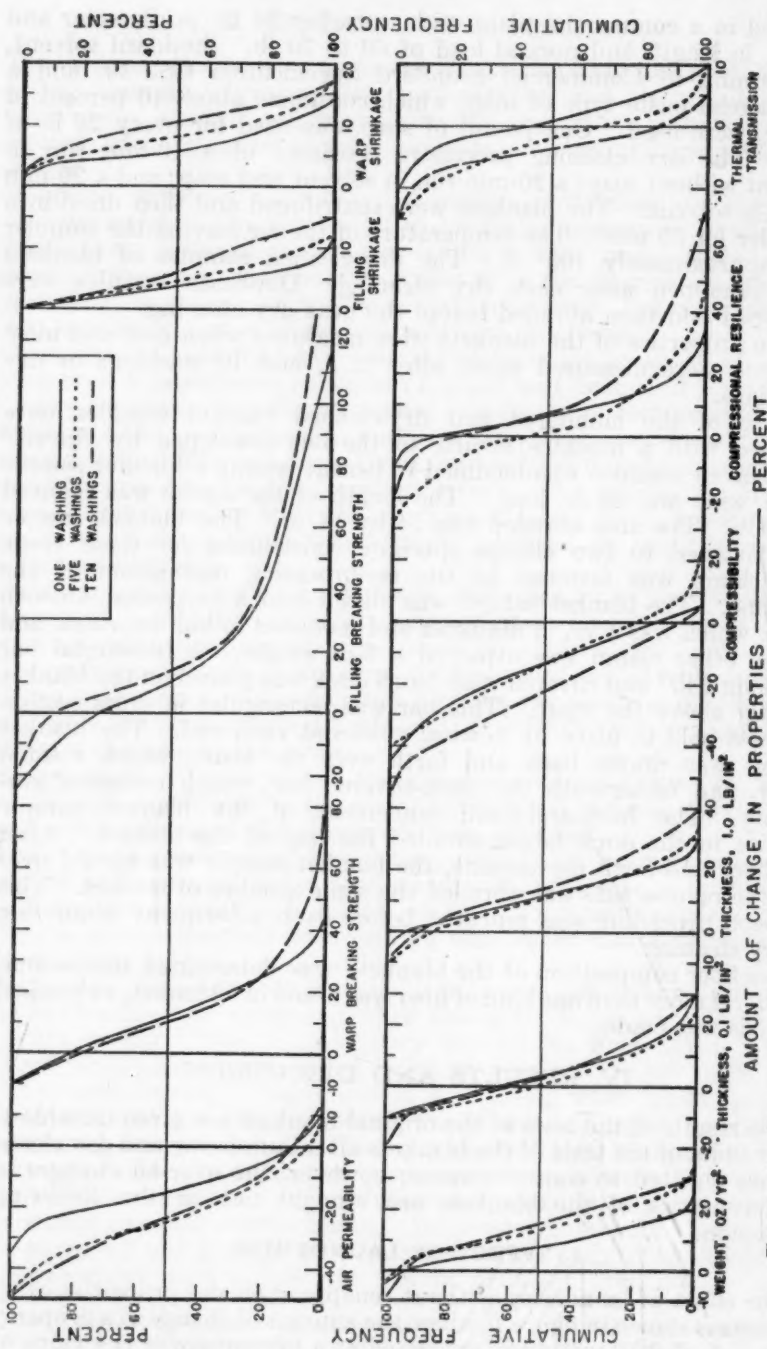

FIGURE 1.—*Frequency with which the blankets changed a given amount in properties after 1, 5, and 10 washings.*

each property the cumulative frequency, expressed as the percentage of blankets that changed more or less than a given amount is plotted as ordinate, the left-hand frequency scale being used for positive changes and the right-hand scale for negative changes. As an example, in 10 washings the areal weight decreased slightly for less than 10 percent of the blankets, whereas half of them increased 15 percent or more in areal weight, and a sixth of them increased in areal weight as much as 25 percent.

All of the blankets shrank in the warp and filling directions when washed. Most of the shrinkage occurred in the first washing, although the shrinkage increased consistently with the number of washings. The shrinkage in the warp direction was approximately twice as great as the shrinkage in the filling direction. The shrinkage of the blankets accounts for their increase in areal weight. It also accounts in part for the increase in breaking strength and thickness and for the decrease in air permeability. In addition to shrinkage, the blankets became felted or matted during washing. This condition is measured by the change in compressibility. A high value for compressibility indicates a greater amount of napping, whereas a low value indicates a greater amount of felting or matting. The considerable decrease in compressibility with the number of washings indicates that the blankets became felted or matted. This change affects the feel to the hands and also the appearance of the blanket. Brushing or renapping of the blanket after washing decreased these changes and restored the blanket more nearly to its condition when new. A blanket which became felted during washing increased in breaking strength and decreased in air permeability.

The compressional resilience of blankets after the fifth washing is appreciably lower than after the first or tenth washing. A high value for compressional resilience indicates greater ability of the blanket to come back to its initial state upon release of a compressive load. The compressional resilience of a blanket will be decreased if the fibers become damaged during use or laundering. This decrease results because damaged fibers have less ability to recover from flexure than undamaged fibers. On the other hand, the compressional resilience of a blanket will increase if it becomes felted during use or laundering. This increase results because there is less motion of the fibers relative to each other when a compressive load is applied owing to the greatly reduced compressibility of a felted blanket. The energy which is lost, frictional forces between fibers times relative movement of fibers, is therefore considerably reduced and the compressional resilience, which is the ratio of the energy recovered when the compressive load is removed to the total energy expended when the compressive load is applied, is increased. The consistent increase in compressional resilience between the fifth and tenth washings resulted from felting of the blankets. The discussion of the change in resilience of a blanket during laundering is general and independent of the kind of fiber. The compressional resilience of a new blanket depends, however, upon the kind of fiber from which it is made. This dependence of resilience upon the fiber composition will be discussed later in this paper.

When a blanket shrinks the thickness at a pressure of 0.10 lb/in.^{2} is increased, and when it becomes felted the density is increased and the thickness at 0.10 lb/in.^{2} is decreased. However, if further shrinkage

FIGURE 1.—*Frequency with which the blankets changed a given amount in properties after 1, 5, and 10 washings.*

occurs during felting the thickness may be increased. As all of these changes occurred when the blankets were washed, the thickness at 0.10 lb/ln.^{2} showed no consistent increase or decrease. This is not true for the thickness at a pressure of 1.0 lb/in.^{2}, because the thickness at this pressure is not greatly affected by felting. Laundering increased the thickness at 1.0 lb/in.^{2}, most of the increase being obtained in the first washing owing to the shrinkage.

The thermal transmission of the blankets was affected little by the number of launderings. None of the blankets increased over 10 percent in thermal transmission, and less than 10 percent of the blankets decreased over 10 percent during the 10 washings. A low value for thermal transmission indicates a high insulating value. In general the thermal transmission of a blanket changes inversely with both thickness and compressibility. Hence if thickness increases while compressibility decreases, the changes tend to annul each other in their effect on thermal transmission. This probably accounts for the fact that the thermal transmission of the blankets is in general affected little by laundering.

The large increase in the filling breaking strength for some 10 percent of the blankets was obtained because they had a low strength when new. These blankets were highly napped and had a high compressibility. It is noteworthy that these initially weak blankets did not become weaker when laundered but became stronger. This increase resulted from the felting and shrinkage produced by laundering.

It is apparent that a number of properties of the blankets changed materially during laundering. Some of the changes, such as the increase in breaking strength, are not objectionable. The smallness of the change in thermal transmission is particularly desirable. However, the rather large decrease in compressibility is objectionable. It denotes a change in the feel and appearance of the blankets. Fortunately, most of this change can be overcome by brushing or renapping of the blanket after washing. This fact is brought out in subsection 2.

2. EFFECT OF LAUNDERING AND RENAPPING, AND OF LAUNDERING, RENAPPING, AND ABRASION

The effects of laundering and renapping; and of laundering, renapping, and abrasion on the properties of 27 blankets are shown in figure 2, where the amount of change in a property after 10 launderings, expressed as a percentage of the value of the property of the blanket when new, is plotted as abscissa, and the cumulative frequency is plotted as ordinate as in figure 1. The changes in a real weight, thickness, thermal transmission, air permeability, breaking strength, and shrinkage are similar in general to the changes shown in figure 1 for laundering without renapping. Compressibility is materially improved by renapping after laundering, whereas compressional resilience is decreased by renapping. The effect of renapping after washing on the appearance of several typical blankets is shown in figures 3 and 4.

The curves showing the changes in the properties of the laundered, renapped, and abraded blankets differ only slightly from the curves for the unabraded blankets. The difference in appearance between the abraded and unabraded blankets was also slight. The weight and thickness of the abraded blanket samples are consistently lower, and

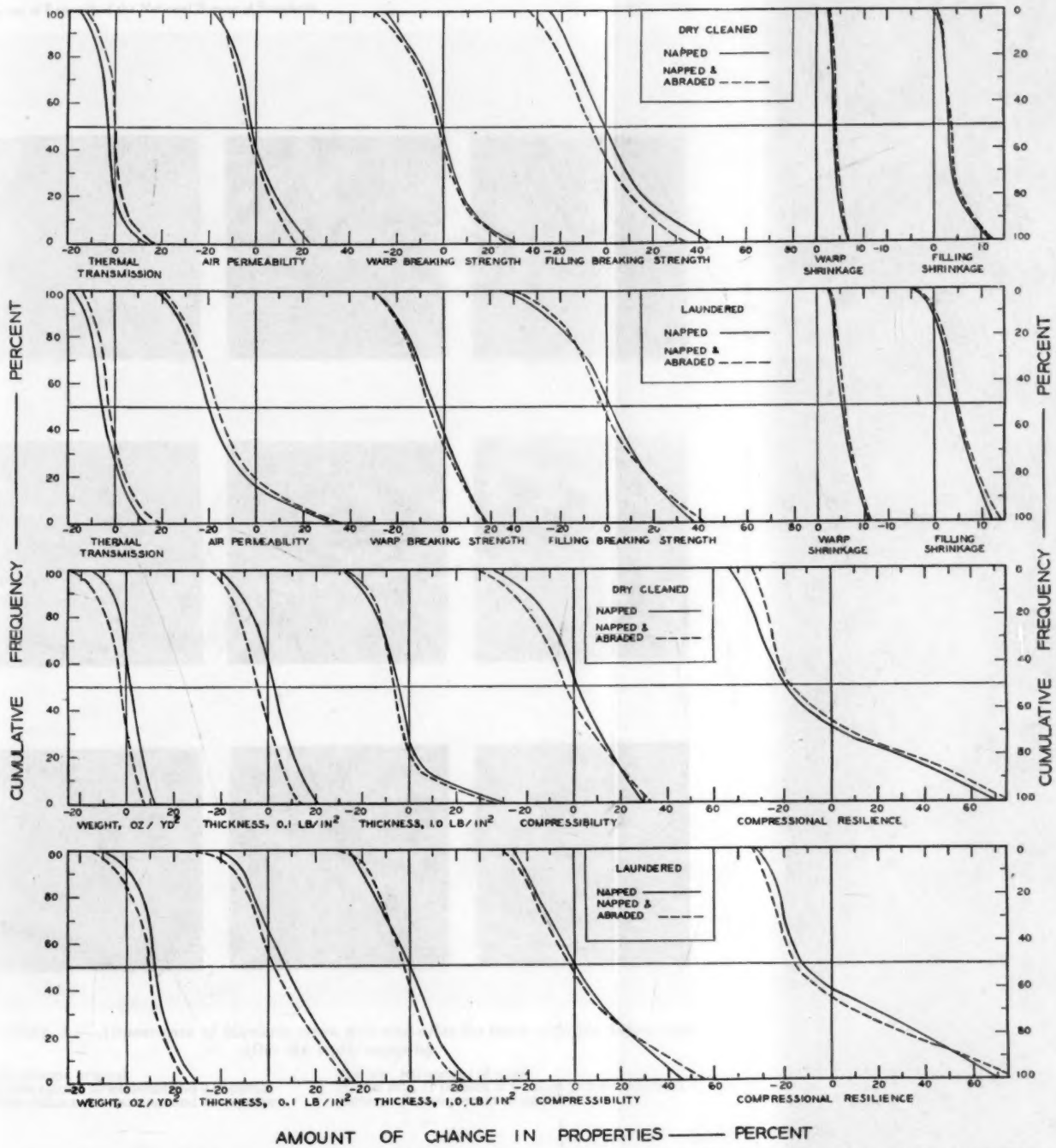

FIGURE 2.—*Frequency with which the blankets changed a given amount in properties after 10 washings and 10 nappings; 10 washings, 10 nappings, and 9 abrasions;10 dry cleanings and 10 nappings; and 10 dry cleanings, 10 nappings, and 9 abrasions.*

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CUMULATIVE FREQUENCY

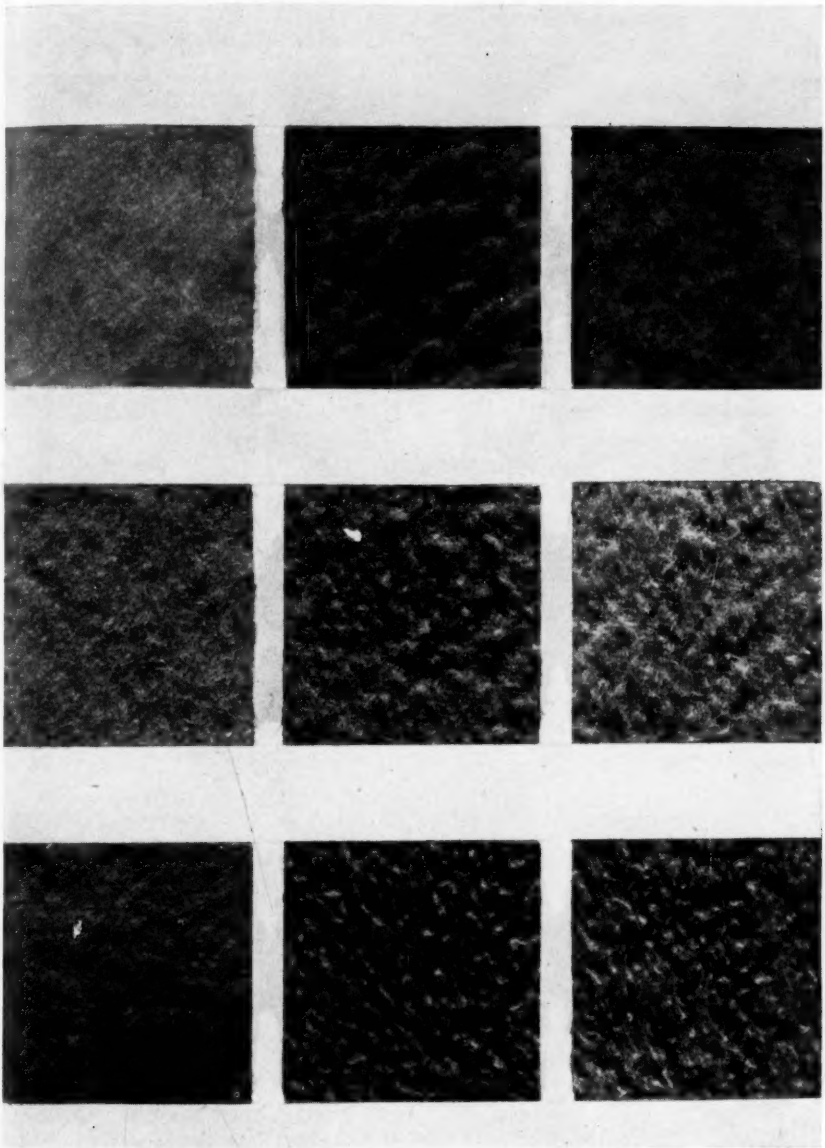

FIGURE 3.—*Appearance of blankets when new and after the tenth washing before and after the tenth napping.*

Left column, original.
Middle colum, 10 washings and 9 nappings.
Right column, 10 washings and 10 nappings.

Top row, 100 percent of wool.
Middle row, 51 percent of wool, 49 percent of cotton.
Bottom row, 100 percent of cotton.

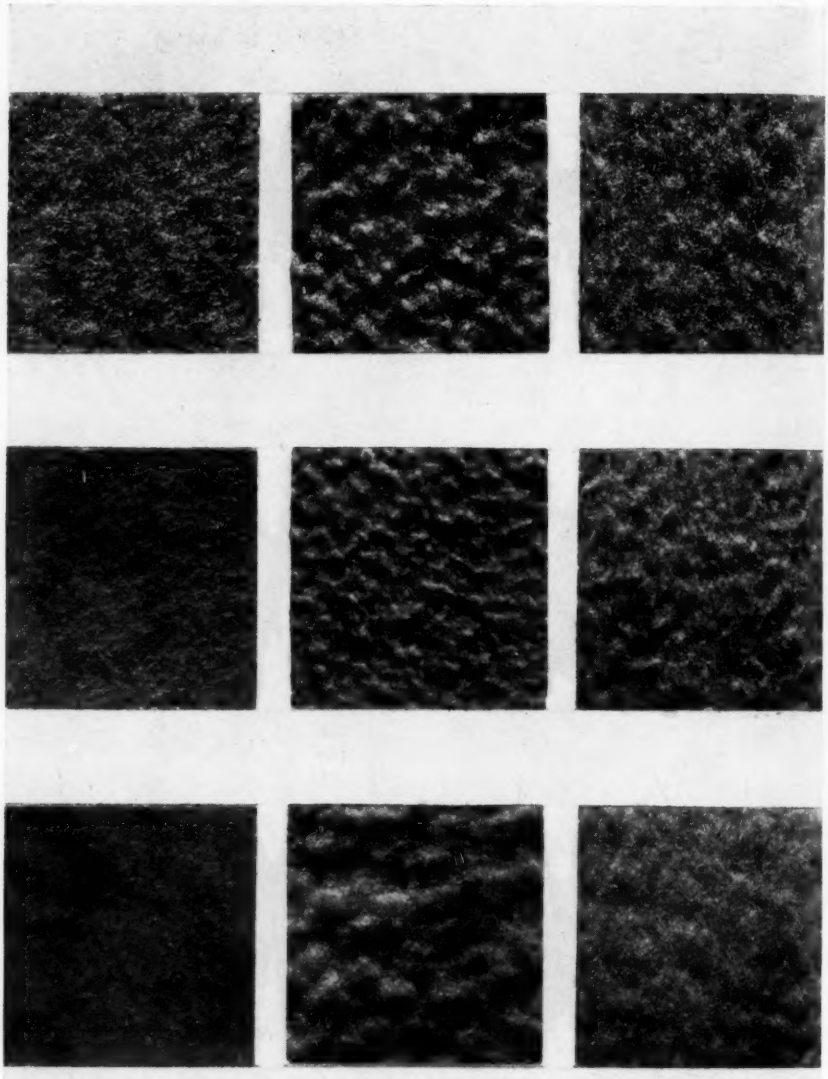

FIGURE 4.—*Appearance of blankets when new and after the tenth washing before and after the tenth napping.*

Left column, original.

Middle column, 10 washings and 9 nappings.

Right column, 10 washings and 10 nappings.

Top row, 23 percent of wool, 31 percent of cotton, 49 percent of viscose rayon.

Middle row, 6 percent of wool, 62 percent of cotton, 32 percent of viscose rayon.

Bottom row, 12 percent of wool, 1 percent of cotton, 87 percent of viscose rayon.

the thermal transmission and air permeability are consistently higher than for the unabraded samples.

3. EFFECT OF DRY CLEANING AND RENAPPING, AND OF DRY CLEANING, RENAPPING, AND ABRASION

The effects of dry cleaning and renapping, and of dry cleaning, renapping, and abrasion on the properties of 27 blankets are also shown by curves in figure 2. These curves show practically the same changes as those for the laundered blankets.

4. EFFECT OF FIBER COMPOSITION ON THE PROPERTIES OF BLANKETS

The blankets in table 1 are listed according to fiber composition. It can be readily seen that there is no correlation between the properties of the blankets and the fiber composition, except for compressional resilience. The average compressional resilience, computed for those blankets having similar fiber composition, is plotted in figure 5 against the wool content. A linear relationship is obtained for blankets containing a mixture of wool and cotton. The difference in compressional resilience between the groups of blankets is statistically highly significant, except between the 5-percent-wool and the all-cotton groups. The addition of 5 percent of wool does not increase the compressional resilience significantly. If a portion of the cotton is replaced with viscose rayon, the compressional resilience is significantly decreased, and if a portion of the cotton is replaced with acetate rayon, the compressional resilience is increased slightly. Several of the 100-percent-wool blankets were known to be made from all-virgin wool. The average compressional resilience of this group was 50 percent, which is higher than the general average of the all-wool blankets. Likewise, a number of blankets were known to be made from a high percentage of reprocessed and reused wool. The average compressional resilience of this group was only 41 percent, which is considerably below the general average of the all-wool blankets. There seems to be a relationship between the compressional resilience of blankets and the quality of wool used. If mechanically damaged wool is used in blankets, the compressional resilience of the blanket is lowered.

5. RELATIONSHIP BETWEEN THERMAL TRANSMISSION AND THICKNESS

The reciprocal of the thermal transmission of blankets and some underwear fabrics recently measured in this laboratory is plotted in figure 6 against the thickness at a pressure of 0.10 lb/in^2. A linear relationship is obtained. Lines indicating 5 and 10 percent deviation are shown in figure 6. The relationship between thermal transmission and thickness is given by equation 1

$$T=\frac{1}{3.0t_{0.1}+0.63}Btu/(°F\ hr\ ft^2), \qquad (1)$$

where T is the thermal transmission, and $t_{0.1}$ is the thickness at a pressure of 0.10 lb/in^2. It will be noted that T is 1.6 when $t_{0.1}$ is zero. This is the value which is obtained when a measurement is made with the bare apparatus. This value of T was used in computing the thermal insulating values given in table 1. The thermal

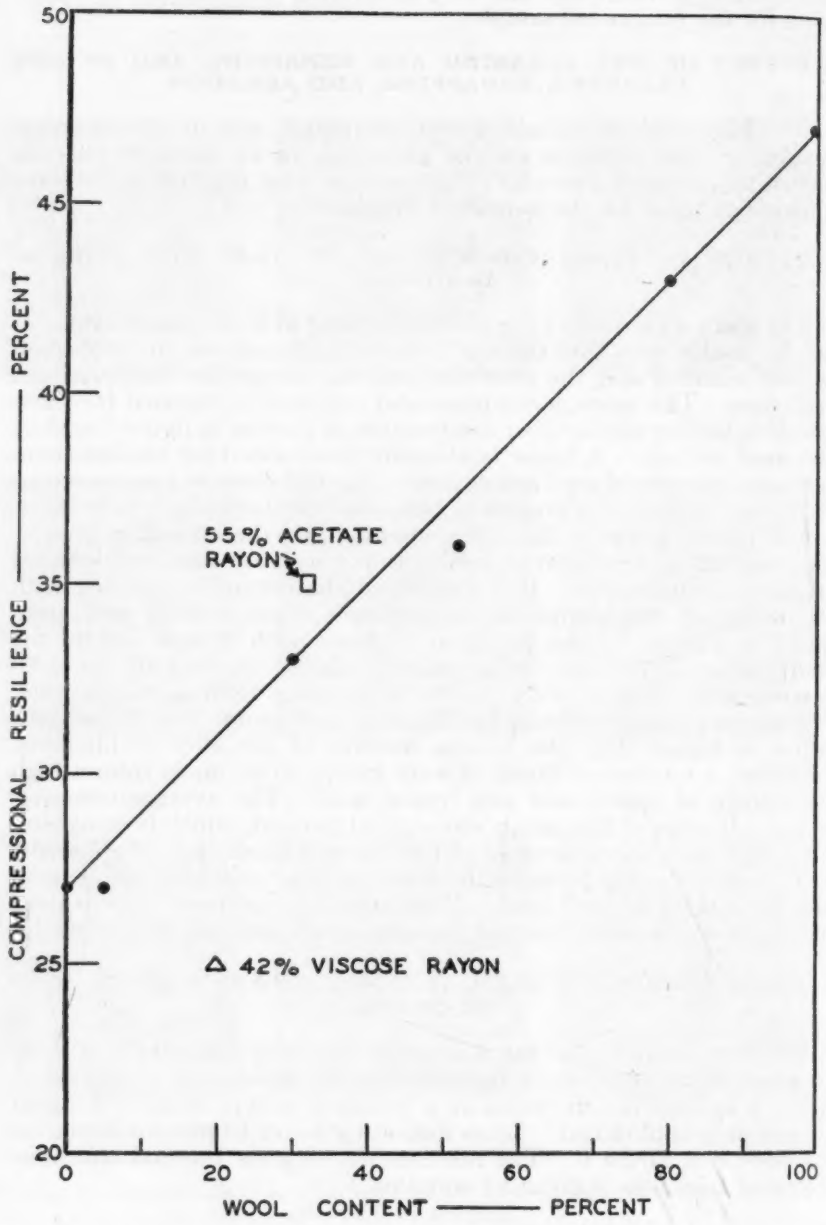

FIGURE 5.—*Linear relationship between compressional resilience and wool content of blankets made from mixtures of wool and cotton.*

Each point represents the average compressional resilience of blankets having approximately the same fiber mixture.

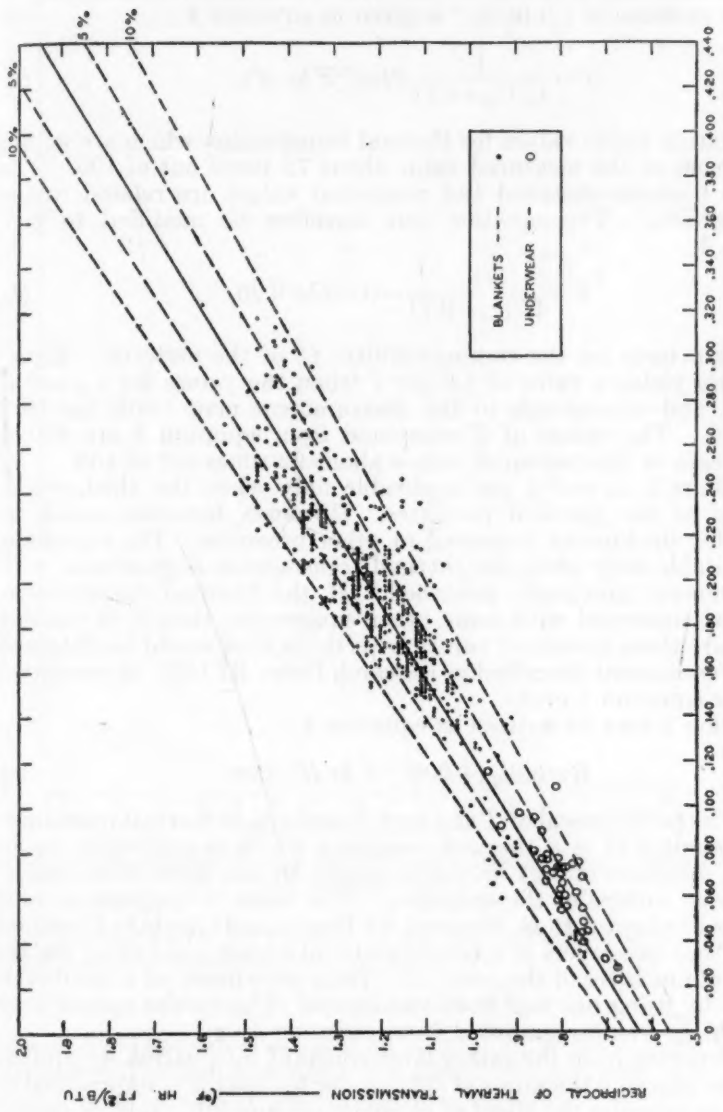

FIGURE 6.—*Linear relationship between the reciprocal of thermal transmission and thickness at 0.10-lb/in.² pressure.*

The dashed lines indicate 5- and 10-percent departures.

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transmission computed by means of equation 1 is within ±10 percent of the measured value about 95 times out of 100. This difference is frequently less than the difference which is obtained when two different portions of one blanket are measured.

The relationship between the thermal transmission and the thickness at a pressure of 1.0 lb/in.[2] is given in equation 2.

$$T=\frac{1}{4.2t_{1.0}+0.71}Btu/(°F\ hr\ ft^2). \tag{2}$$

This equation yields values for thermal transmission which are within ±10 percent of the measured value about 75 times out of 100. The residuals between observed and computed values are related to the compressibility. The equation can therefore be modified to give equation 3,

$$T=\frac{1}{4.2t_{1.0}+0.71}-0.65C+0.20, \tag{3}$$

including a term for the compressibility, C, of the material. Equation 3 also yields a value of 1.6 for T when the values for $t_{1.0}$ and C are zero, and corresponds to the measurement made with the bare apparatus. The values of T computed from equation 3 are within ±10 percent of the measured values about 92 times out of 100.

Equations 1, 2, and 3 are applicable only when the thickness is measured at the specified pressures. However, formulas could be derived for thicknesses measured at other pressures. The equations are applicable only when the thermal transmission is measured with the equipment previously described.[8] If the thermal transmission values are measured with some other equipment, then it is possible to compare these measured values with those that would be obtained with the equipment described in Research Paper RP1055, as computed by either equation 1 or 3.

Equation 1 may be written as equation 4,

$$R=3.0t_{0.1}+0.63(°F\ hr\ ft^2)/Btu, \tag{4}$$

where R is the reciprocal of T and may be defined as thermal resistance. The constant 0.63 is a thermal resistance which is equivalent to an effective thickness of 0.21 in. and is caused by the layer of still air at the exposed surface of the specimen. This value is comparable with the value of about 0.16 in. reported by Baxter and Cassie.[9] Equation 4 shows that two layers of a textile material do not yield twice the insulation of one layer of the material. Tests were made on a number of blankets by using one and then two layers. The results agreed very well with the values computed from equation 4 or 1.

It is apparent from the rather large constant in equation 4, equivalent to an effective thickness of 0.21 in. for $t_{0.1}$, that it is impractical to attempt to measure the effect of construction and other factors on the thermal resistance of thin materials, such as light underwear and dress fabrics, since the thermal resistance contributed by thin fabrics may amount to only some 10 to 20 percent of that of the layer of still air.

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[8] R. S. Cleveland, J. Research NBS **19**, 675 (1937) RP1055.
[9] *Thermal insulating properties of clothing*, J. Textile Inst. **34**, No. 7, T41-T54 (July 1943).

6. RELATIONSHIP BETWEEN WEIGHT AND THICKNESS

A linear relationship between thickness and areal weight is often assumed or taken for granted. It is shown in figure 7, however, that

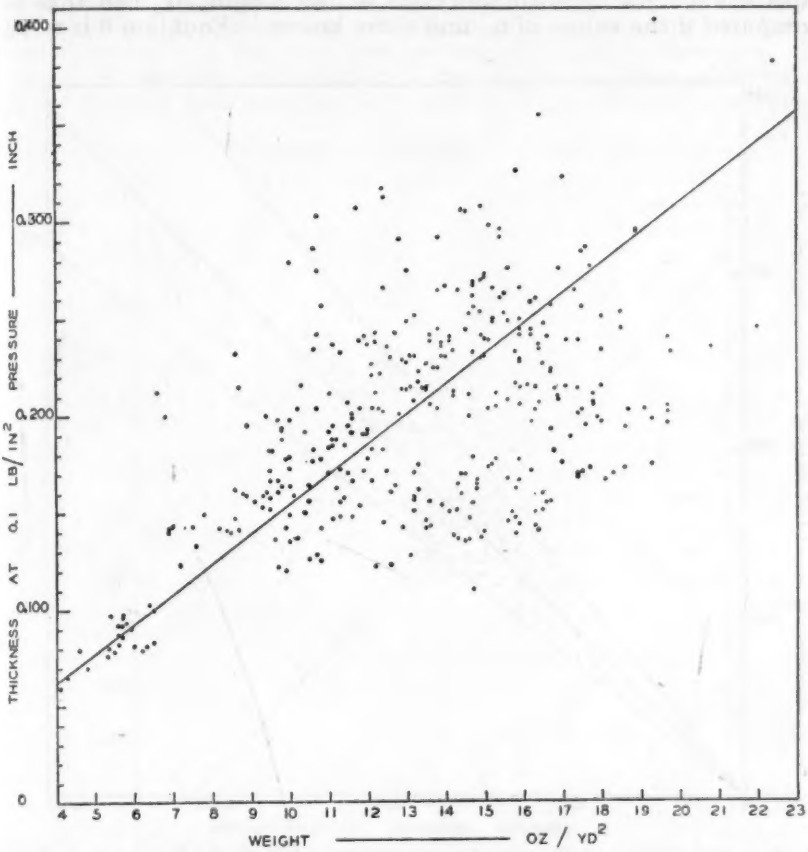

FIGURE 7.—*Relationship between the thickness of blankets at 0.10-lb/in.² pressure and the weight.*

such a correlation is very poor. The best straight line through the plotted points corresponds to equation 5

$$t_{0.1}=0.0155W, \tag{5}$$

in which $t_{0.1}$ is the thickness at 0.10 lb/in.², and W is the areal weight A further study indicates that the points are scattered about this line in a manner closely associated with the compressibility. If the ratio of the observed values of $t_{0.1}$ to the values computed by means of equation 5 are plotted against compressibility, an approximate linear relationship is obtained. Equation 5 can thus be modified to yield equation 6,

$$t_{0.1}=0.05CW, \tag{6}$$

where C is the compressibility.

If the thicknesses of the blankets computed by means of equation 6 are plotted against the measured values, figure 8, a straight line with unit slope is obtained. The points, although still scattered considerably, lie for the most part within ±20 percent of the line given by equation 6. An approximate value of the weight, W, can thus be computed if the values of $t_{0.1}$ and C are known. Equation 6 is useful

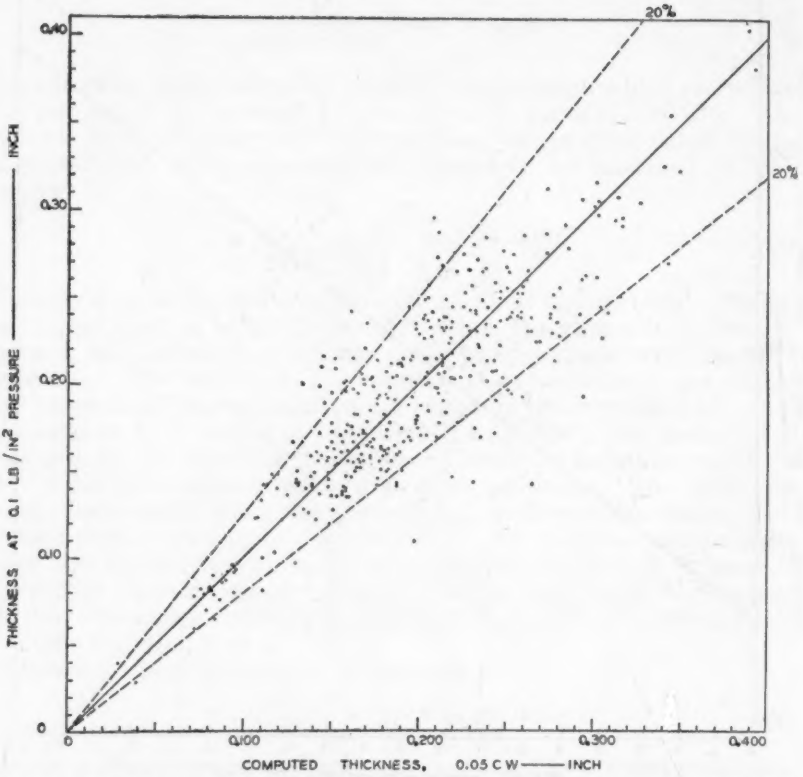

FIGURE 8.—*Linear relationship between the thickness of blankets at 0.10 lb/in.² pressure, $t_{0.1}$, and the thickness computed from the weight, W, and the compressibility, C, by the equation $t_{0.1}=0.05CW$.*

The dashed lines indicate a 20-percent departure.

as a guide in specifying minimum compatible requirements for a performance specification for blankets.

7. RELATION OF STRENGTH TO WEIGHT AND TO COMPRESSIBILITY

The breaking strength of blankets was found to increase in general with the areal weight and to decrease with the compressibility. Although the functional relationships between strength and areal weight and between strength and compressibility are not well defined, they suffice for use as a guide in specifying minimum requirements for a performance specification of blankets that will be compatible with the other requirements and also provide reasonable assurance of satisfactory performance.

8. RELATIVE THERMAL INSULATION PER UNIT WEIGHT

The reciprocal of thermal transmission has been used as a measure of the relative thermal insulation of textiles. This value divided by the areal weight of the material has been used to indicate the efficacy as an insulating material and is given in table 1. It can be readily seen that it varies with the thickness but not with fiber composition. In general, the greater the thickness of the blanket the lower is the value of the thermal resistance per unit weight. The correlation, however,

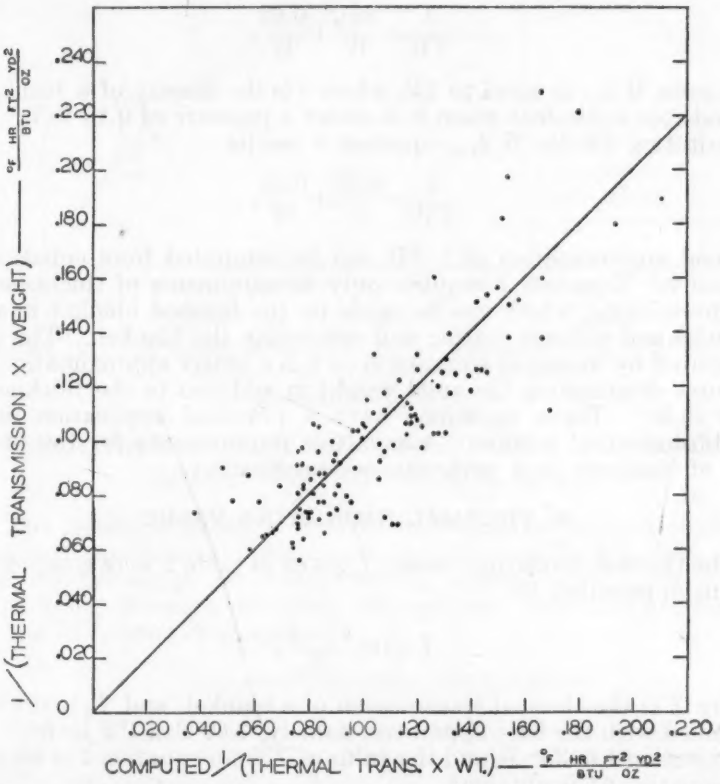

FIGURE 9.—*Linear relationship between the reciprocal of thermal transmission times weight and the value computed by means of equation 7.*

is far from good for the blankets as a group. The correlation is greatly improved if the blankets are grouped according to their compressibility. The general relation can be expressed by equation 7, where T is thermal transmission, W is weight, C is compressibility,

$$\frac{1}{TW}=0.4C-0.4t_{0.1}+0.05, \tag{7}$$

and $t_{0.1}$ is thickness at 0.10 lb/in². The values of $1/TW$ computed by means of equation 7 are plotted in figure 9 against the values computed from the measured values of T and W. The points lie fairly close to a straight line having a slope of unity. This indicates that equation 7 represents the data fairly well.

The physical significance represented by equation 7 is not immediately apparent, except that the relative thermal insulation of blankets per unit weight depends upon the thickness and compressibility and therefore upon the structure of the blanket. However, the compressibility and thickness of a blanket of a given weight are inversely related to the density. The relative thermal insulation per unit weight given by equation 7 is therefore inversely related to the density. This relationship can be derived directly from equation 1 or 4 and is given by equation 8.

$$\frac{1}{TW}=\frac{3t_{0.1}}{W}+\frac{0.63}{W}, \tag{8}$$

The ratio $W/t_{0.1}$ is equal to 12δ, where δ is the density of a blanket in pounds per cubic foot when it is under a pressure of 0.10 lb/in^2. By substituting 12δ for $W/t_{0.1}$, equation 9 results.

$$\frac{1}{TW}=\frac{0.25}{\delta}+\frac{0.63}{W}, \tag{9}$$

A good approximation of $1/TW$ can be computed from equations 7, 8, and 9. Equation 7 requires only measurements of thickness and compressibility, which can be made on the finished blanket in a few minutes and without cutting and destroying the blanket. The value computed by means of equation 8 or 9 is a better approximation, but requires determining the areal weight in addition to the thickness at 0.10 lb/in^2. These equations have a practical application in the establishment of minimum compatible requirements for the properties of blankets in a performance specification.

9. THERMAL INSULATING VALUE

The thermal insulating values, I, given in table 1 were computed by means of equation 10

$$I=100\frac{T_b-T}{T_b}, \tag{10}$$

where T is the thermal transmission of a blanket, and T_b is the value obtained with the bare apparatus, namely, 1.60 Btu/(°F hr ft^2). By substituting 1.60 for T_b and the value of T from equation 1 in equation 10, equation 11 is obtained,

$$I=\frac{100}{1+0.21/t_{0.1}}, \tag{11}$$

where $t_{0.1}$ is the thickness at a pressure of 0.10 lb/in^2. In figure 10 the values of I from table 1 are plotted against $t_{0.1}$ and the curve shown is the locus of equation 11. The thermal insulating value obtained for underwear fabrics, blankets, and several lined jackets agree very well with the curve representing equation 11. It can be readily seen that the thermal insulating value of textiles having the same thickness, $t_{0.1}$, as measured in this investigation, does not depend upon the fiber composition and type of fabric construction. A very good value of I can be computed with equation 11 if the value of

$t_{0.1}$ is known. This value of a fabric or garment is readily measurable and does not require cutting or destroying the material for the test.

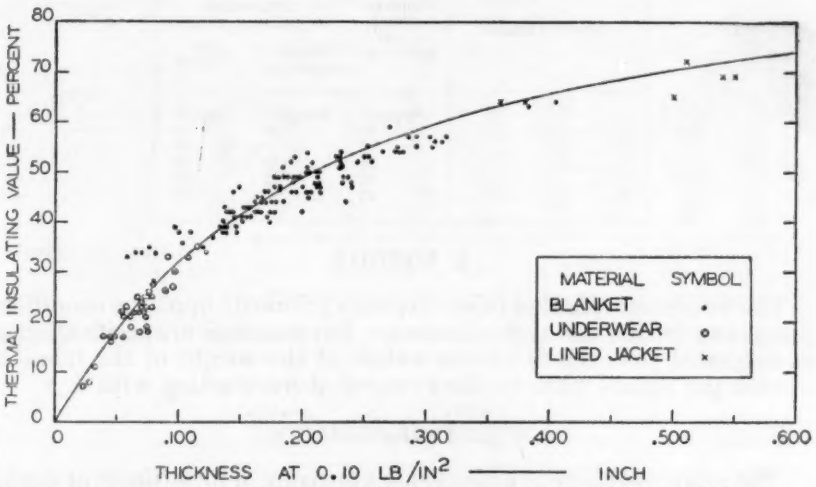

FIGURE 10.—*Relationship between the thermal insulating value, I, of blankets and the thickness, $t_{0.1}$ at 0.10-lb/in² pressure.*

The curve represents equation 11.

V. SUGGESTED REQUIREMENTS FOR A PERFORMANCE SPECIFICATION FOR BLANKETS

The results obtained in this investigation can be used as the basis for the preparation of performance specifications for blankets. Limits for compressional resilience, weight, compressibility, thickness at 0.10 lb/in.² pressure, breaking strength, and shrinkage are suggested in the following paragraphs.

1. COMPRESSIONAL RESILIENCE

A soft, fluffy, flexible, and warm blanket having a high compressional resilience is expected to retain these characteristics more nearly during use than one having a low compressional resilience. The compressional resilience was found to be linearly related to the fiber composition of blankets containing cotton and wool. It could therefore serve as a requirement in a performance specification in place of fiber composition, since it is readily measured without cutting or destroying a blanket. The minimum values suggested for a performance specification are given in table 2. The approximate fiber composition corresponding to the suggested values for compressional resilience is indicated. The suggested values for compressional resilience are applicable to blankets regardless of their weight.

TABLE 2.—*Suggested values of compressional resilience for use in a performance specification*

Type of blanket	Minimum compressional resilience	Approximate fiber composition	
		Wool, minimum	Cotton
	Percent	*Percent*	*Percent*
A	45	90	10
B	40	65	35
C	35	40	60
D	30	15	85
E	25	----------	100

2. WEIGHT

The weight of a blanket fabric depends primarily upon the conditions prevailing for the use of the blanket. For purposes of specification, it is suggested that the minimum values of the weight of the fabric in ounces per square yard be the even numbers, starting with 4.

3. COMPRESSIBILITY

The compressibility of a blanket is a measure of its loftiness or degree of napping. The values to be specified depend again upon the conditions of intended use and also upon individual preferences for the feel and appearance of blankets. For purposes of specification, it is suggested that the minimum values specified be in increments of 0.05 beginning with 0.20 (in./in.)/(lb/in^2). A blanket having a low compressibility is one which is greatly felted, little napped, and stiff, or boardy, and one having a high compressibility is lofty, soft, highly napped, and flexible.

4. THICKNESS

The thickness of a blanket is probably the most important characteristic to be specified in a performance specification. It has been shown that the thermal transmission and the thermal insulationg value correlate exceedingly well with the thickness at 0.10 lb/in^2. Simple formulas, equations 1 and 11, have been derived for calculating these values from this thickness. Minimum values for thickness are suggested in table 3 for various weights and compressibilities in preference to either thermal transmission or thermal insulating values, because of the ease of measurement of thickness which is obtained when the measurements for compressional resilience and compressibility are made, and because the thickness can be measured without the need of cutting or destroying the blanket. However, computed thermal transmission and thermal insulating values are given in table 4 for different thicknesses as a guide for converting the thickness values of table 3 to these quantities. The densities in pounds per cubic foot at a pressure of 0.10 lb/in.^{2} are given in table 3 for information and correspond to blankets having different compressibility.

TABLE 3.—*Minimum thickness at 0.10 lb/in.² suggested for blankets of various weights and compressibilities*

Weight	Compressibility, $\frac{\text{in./in.}}{\text{lb/in.}^2}$								
	0.20	0.25	0.30	0.35	0.40	0.45	0.50	0.55	0.60
oz/yd²	*in.*	*in.*	*in.*	*in.*	*in.*	*in.*	*in.*	*in.*	*in.*
4	0.040	0.050	0.060	0.070	0.080	0.090	0.100	0.110	0.120
6	.060	.075	.090	.105	.120	.135	.150	.165	.180
8	.080	.100	.120	.140	.160	.180	.200	.220	.240
10	.100	.125	.150	.175	.200	.225	.250	.275	.300
12	.120	.150	.180	.210	.240	.270	.300	.330	.360
14	.140	.175	.210	.245	.280	.315	.350	.385	.420
16	.160	.200	.240	.280	.320	.360	.400	.440	.480
18	.180	.225	.270	.315	.360	.405	.450	.495	.540
Density, lb/ft³, at 0.10 lb/in.²	8.3	6.7	5.5	4.8	4.2	3.7	3.3	3.0	2.8

TABLE 4.—*Thermal transmission and thermal insulating values corresponding to various thicknesses at 0.10 lb/in.²*

Thickness at 0.10 lb/in.²	Thermal transmission	Thermal insulating value
in.	*Btu/(°F hr ft²)*	*Percent*
0.010	1.52	4.5
.020	1.45	8.7
.040	1.33	16
.060	1.23	22
.080	1.15	28
.100	1.08	32
.125	1.00	37
.150	0.93	42
.175	.87	45
.200	.81	49
.250	.72	54
.300	.65	59
.350	.60	62
.400	.55	66
.450	.50	68
.500	.47	70
.550	.44	72
.600	.41	74

5. BREAKING STRENGTH

The breaking strength was found to be related to the weight and to the compressibility of a blanket. Minimum values for breaking strength (grab method) of the warp and filling for blankets of various weights and compressibilities are suggested in table 5. Manufacturers should have no difficulty in meeting the strength requirements suggested. Most blankets meeting the other requirements will exceed the suggested values for breaking strength. Furthermore, since blankets generally increased in breaking strength during laundering, it is believed that the values suggested in table 5 will assure satisfactory performance of the blankets for ordinary use.

TABLE 5.—*Minimum breaking strength (grab method) suggested for blankets of various weights and compressibilities*

Weight	Warp strength			Filling strength		
	Compressibility, in./in. / lb/in.²			Compressibility, in./in. / lb/in.²		
	Below 0.25	0.25 to 0.35	Above 0.35	Below 0.25	0.25 to 0.35	Above 0.35
oz/yd²	lb	lb	lb	lb	lb	lb
4	25	20	15	15	10	5
6	30	25	20	20	15	10
8	35	30	25	25	20	15
10	40	35	30	30	25	20
12	45	40	35	35	30	25
14	50	45	40	40	35	30
16	55	50	45	45	40	35
18	60	55	50	50	45	40

6. AIR PERMEABILITY

No requirements are suggested for air permeability, since in general blankets will be used in nominally still air. For outdoor uses a combination of blanket-and-wind resistant cloth has decided advantages.[10]

7. SHRINKAGE

The maximum allowable shrinkage suggested is 5 percent in the warp and in the filling. This amount of shrinkage is to be expected in normally manufactured blankets. Proper precautions in laundering blankets to preserve their characteristics should automatically safeguard against excessive and objectionable shrinkage. It seems advisable to specify nominal dimensions of the blankets 5 percent greater than necessary so that the blankets will not be too small after a shrinkage of 5 percent.

WASHINGTON, December 28, 1943.

[10] Herbert F. Schiefer, *Advantages of a blanket-and-sheet combination for outdoor use*, J. Research NBS 30, 209 (1934) RP1529.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1590

Part of Journal of Research of the National Bureau of Standards, Volume 32, June 1944

STUDIES OF PORTIONS OF THE QUATERNARY SYSTEM SODA-LIME-SILICA-WATER AT 25° C

By George L. Kalousek

ABSTRACT

A study has been made of portions of the system soda-lime-silica-water at 25° C. The only solid phases found were $Ca(OH)_2$ and a four-component gel of variable composition. The boundary, $Ca(OH)_2$—soda-lime-silicate gels, was determined and the compositions of the gels along this boundary shown to vary from $0.003Na_2O:2.0CaO:1.0SiO_2:xH_2O$ (at 0.2 g of Na_2O per liter) to about $0.25Na_2O:1.0CaO:1.0SiO_2:xH_2O$ (at 20 g per liter and extending to 101 g per liter of Na_2O). In regions off the boundary, at selected constant concentrations of Na_2O but with increasing concentrations of SiO_2 in solution, the $Na_2O:SiO_2$ molar ratio of the gels varied only slightly from 0.2 in most cases; the $CaO:SiO_2$ molar ratio, however, decreased to values approaching 0.1 at the maximum concentrations of SiO_2 used. Interpretations pertaining to relations between the composition of the gels and solutions are given.

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I. INTRODUCTION

The role of the alkalies, soda and potash, in hydrating cements is not fully understood. Information on how these constituents alter the chemical composition of the lime silicate hydrates and of other products in hydrating cements should be highly useful in explaining the mechanism of the various hydration processes involved. Also, a knowledge of the compositions of the alkali solutions in which the hydrated cement compounds are stable should prove helpful in elucidating the effects of the alkalies on hydrating cements in the presence of "reactive" aggregates.

The present investigation was accordingly designed for obtaining a portion of such data and was concerned with the effects of Na_2O on the compositions of the lime silicate hydrates and of the aqueous phase in which they are stable. The investigation was essentially a study of portions of the quaternary system soda-lime-silica-water at 25° C.

II. MATERIALS

The starting materials were solutions of sodium silicate and sodium hydroxide of known compositions, crystals of $Ca(OH)_2$ and distilled water.

The sodium silicate solution was a reagent-quality product containing not more than 0.2 percent of CO_2 and having a molar ratio of $1.00Na_2O{:}3.34SiO_2$. Sodium hydroxide was freed of carbonate by preparing a saturated solution. The clear supernatant liquid was drawn off and diluted as required.

Calcium hydroxide of reagent quality and having a particle size of less than 1 micron was used for most of the experiments. Also, $Ca(OH)_2$ crystals of varying sizes, prepared by adding solutions of NaOH to saturated solutions of $Ca(OH)_2$, were used in a number of exploratory preparations.

III. PROCEDURE

1. PREPARATION AND FILTRATION OF MIXTURES

A few tentative mixtures of the standard solutions and the $Ca(OH)_2$ were made in order to establish the amounts required to produce the desired quantities (about 0.5 to 1.0 g) of the precipitates in mixtures having a volume of 200 ml. Most of the mixtures were made by adding a solution of sodium silicate to a well-agitated suspension of fine-grained $Ca(OH)_2$ in a solution of NaOH. The resulting preparations in tightly stoppered ceresin-lined flasks were stored in an air bath maintained at 25 ± 0.05° C until filtered at ages ranging from 2 to 18 weeks. During the first 5 to 8 hours after mixing the preparations, they were shaken about once each hour, and then once daily after the first day. Although this was the general procedure followed, it will be necessary, as required in certain sections of this report, to give more specific details.

The time allowed the mixtures to "age" was selected arbitrarily. It may be mentioned, however, that neither the solid phase nor solution underwent any determinable changes in time periods of from several weeks to several months. It is recognized that this steady state may be displaced by eventual crystalization of the solid phase, a process which, however, appears to proceed exceedingly slowly at room temperature.

The mixtures were filtered through a medium-textured sintered glass crucible by application of suction. The residue on the filter during the last stages of filtration was firmly compacted with a rubber plunger, and as much of the solution was withdrawn as permitted by the retentivity of the gelatinous precipitate. The precipitate was next redispersed in a small amount of wash solution (ethyl alcohol and water or water if the filtrate contained more than 70 g of SiO_2 per liter) and the solution again filtered off. The most suitable ratio of alcohol to water for each wash solution was determined by testing a

few milliliters of the original filtrate and selecting the maximum alcohol content which just failed to produce a suspension. Four to five successive washings were made with solutions of progressively increasing alcohol content, then four to five washings with 95-percent ethyl alcohol, and finally four to five washings with ethyl ether. In the course of each washing, the precipitate was redispersed and during filtration, compacted on the filter. After being washed the precipitate was left in the laboratory air for 1 day and then stored in a tightly stoppered vial.

2. METHODS OF CHEMICAL ANALYSES

Standard procedures of chemical analyses were followed. All of the solutions and most of the precipitates were analyzed for soda, lime, and silica. The "hydrate" water of the precipitates was determined by difference.

The amounts of Na_2O in the filtrates containing relatively small amounts of SiO_2 (1 percent or less of the total solids) were determined by titrating the solutions with HCl, using methyl red as indicator. Allowance was made for the $Ca(OH)_2$ present, which was determined gravimetrically. The errors in the results were not greater than 1 percent of the amount of Na_2O, as determined occasionally for check purposes by precipitation. In all the other determinations, the Na_2O, after removal of SiO_2, was precipitated and weighed as sodium zinc uranyl acetate hydrate.

Calcium was precipitated as oxalate, ignited, and weighed as CaO. However, when the filtrates contained over 50 g of Na_2O per liter the CaO was precipitated as phosphate, converted to sulfate, and reprecipitated as oxalate according to the method described by Hillebrand Lundell [1].[1] In the analysis for SiO_2 the solutions were dehydrated twice with HCl. The combined residues were ignited to constant weight and treated with HF. The loss in weight was reported as SiO_2.

IV. RESULTS AND DISCUSSION

1. PRELIMINARY OBSERVATIONS

Exploratory mixtures showed that only gelatinous precipitates were formed. Some of these, in mixtures of high concentrations of SiO_2, were highly solvated gels and others, in mixtures of high concentrations of Na_2O and low concentrations of SiO_2, appeared as grains of gel. Analyses indicated that the $CaO:SiO_2$ molar ratio of the gels decreased as the concentration of Na_2O in solution was increased and the $Na_2O:SiO_2$ molar ratios were found to increase up to a certain value. At constant concentrations of Na_2O in solution, but with increasing amounts of SiO_2, the $CaO:SiO_2$ ratios were found to decrease. The four-component gelatinous products are referred to as soda-lime-silicate gels, or, more often, simply as gels.

The shifts in the compositions of the gels could not be followed microscopically as the changes in the indices were small and appeared to be affected by aging. The presence or absence of small amounts of fine-grained crystals of $Ca(OH)_2$ could not be ascertained reliably by means of the microscope. Large crystals of $Ca(OH)_2$ could not be

[1] Figures in brackets indicate the literature references at the end of this paper.

used as they were converted but slowly to the siliceous products owing to the formation of gelatinous deposits around the crystals.

2. BOUNDARY, $Ca(OH)_2$—SODA-LIME-SILICATE GELS

Considerations based on the preliminary results indicated that the best initial procedure to follow in studying the system would be to ascertain the compositions of the aqueous phase in contact with $Ca(OH)_2$ and the soda-lime-silicate gels. Accordingly, the mixtures for establishing this boundary were prepared, only a moderate excess of crystalline $Ca(OH)_2$ being used. The concentration of Na_2O was varied from 0.2 to 152 g per liter. After 2 to 7 weeks, the mixtures were filtered and the filtrates and precipitates analyzed.

All the data pertaining to the mixtures, filtrates, and precipitates are reported in table 1, the compositions of the solutions being given in grams per liter of Na_2O, CaO, and SiO_2. The table shows that the amount of CaO in solution decreased from 0.92 to about 0.02 g per liter as the concentration of Na_2O was increased from 0.2 to about 20 g per liter. Simultaneously, the concentrations of SiO_2 increased from 0.002 to about 0.020 g per liter. In the range of concentrations of Na_2O from 20 to 152 g per liter, the amounts of CaO in solution remained nearly constant at a value of about 0.010 g per liter, but those of SiO_2 increased from 0.02 to over 1.1 g per liter.

Figure 1 shows the g per liter of CaO and SiO_2 found in solution at the different concentrations of Na_2O.

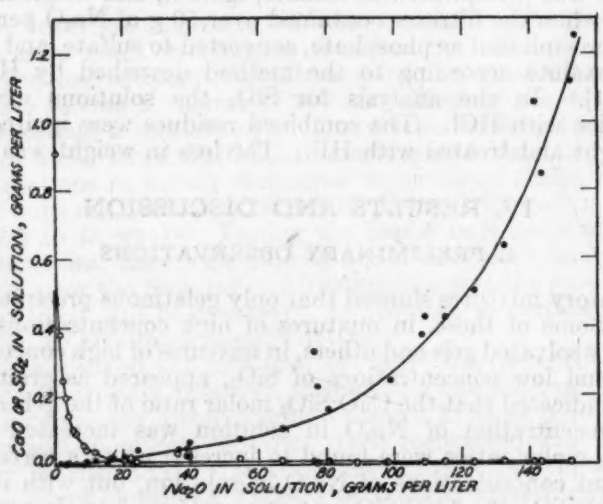

FIGURE 1.—*Amounts of* Na_2O, CaO, *and* SiO_2 *in filtrates from mixtures containing solid* $Ca(OH)_2$ *and soda-lime-silicate gels.*

○=CaO

●=SiO_2

TABLE 1.—*Compositions of solutions in contact with crystalline* $Ca(OH)_2$ *and soda-lime-silicate gels and the compositions of the mixed solids*

No.	Composition of Mixtures in grams per liter			Age in weeks	Composition of solutions in grams per liter			Molar compositions of mixed solids				
									From direct analyses			
	Na_2O [a]	CaO	SiO_2		Na_2O	CaO	SiO_2	Computed CaO:SiO_2	Na_2O	CaO	SiO_2	H_2O
1	2.0	1.864	0.655	4	1.69	0.380	0.001	2.43	0.03	2.42	1.00	------
2	3.5	1.490	.655	4	3.16	.195	.001	2.12	.05	2.09	1.00	------
3	4.5	1.248	.655	7	4.00	.140	.006	[b] 1.83	.05	1.69	1.00	------
4	6.5	1.116	.655	4	6.17	.090	.002	1.69	.12	1.60	1.00	------
5	9	0.932	.655	4	8.74	.055	.002	1.43	.13	1.38	1.00	3.3
6	13	.745	.655	4	12.00	.037	.011	1.18	.18	1.18	1.00	3.0
7	16	.947	.655	7	15.30	.029	.008	1.52	.18	1.49	1.00	------
8	18	.655	.640	4	17.8	.019	.015	1.09	.22	1.09	1.00	3.3
9	21	.618	.640	4	20.6	.013	.026	1.06	.22	1.03	1.00	2.9
10	25	.596	.655	4	24.3	.009	.043	1.03	.23	1.02	1.00	3.1
11	37	1.490	1.310	6	36.5	.038	.046	1.23	.23	1.25	1.00	2.9
12	40	0.945	0.655	2	39.0	.028	.048	[b] 1.63	.29	1.31	1.00	3.6
13	40	.851	.655	5	39.6	.025	.065	1.40	------	------	------	------
14	55	1.490	1.310	6	54.5	.018	.071	1.24	.26	1.26	1.00	3.2
15	68	1.490	1.310	6	67.0	.011	.106	1.32	.25	1.34	1.00	3.0
16	77	0.605	0.655	2	76.2	.008	.325	[b] 1.93	.23	1.08	1.00	3.0
17	78	.606	.655	5	77.4	.004	.227	1.51	------	------	------	------
18	82	1.490	1.310	6	80.8	.010	.157	1.38	.25	1.37	1.00	3.0
19	100	1.490	1.310	6	99.0	.004	.241	[b] 1.49	.24	1.36	1.00	2.9
20	110	0.932	1.310	7	108.1	.006	.377	1.07	.27	1.02	1.00	2.7
21	110	.756	1.192	2	109	.004	.428	1.05	.24	1.06	1.00	3.0
22	116	.932	1.310	6	115.0	.008	.424	1.09	------	1.12	1.00	2.7
23	125	.932	1.310	6	123.5	.010	.501	1.22	.29	1.26	1.00	3.2
24	135	.932	1.310	6	132.5	.006	.633	1.46	.25	1.43	1.00	3.2
25	144	.380	1.310	3	141.6	.005	1.058	1.60	.19	1.55	1.00	------
26	145	.932	1.638	5	143.5	.006	0.845	1.27	.26	1.26	1.00	2.9
27	155	.932	1.965	5	152.0	.007	1.131	1.18	.26	1.16	1.00	2.6
28	155	.530	1.310	5	153.1	.00	1.250	------	------	------	------	------

[a] The amount of Na_2O added is approximate in these preparations.
[b] $Ca(OH)_2$ separated partly from mixture of solids.

(a) COMPOSITIONS OF SODA-LIME-SILICATE GELS

The precipitates obtained in the mixtures used for locating the boundary, although containing $Ca(OH)_2$, were suitable for ascertaining the Na_2O:SiO_2 molar ratios of the soda-lime-silicate gels.

The compositions of the precipitates, assigning a value of unity to the mols of SiO_2, are given in table 1 (last four columns) as the molar ratios of Na_2O:CaO:SiO_2:H_2O. Thus, the column under Na_2O gives the molar ratio of Na_2O:SiO_2 of the gels.

The molar ratios of CaO to SiO_2 of gels along the boundary could not be determined reliably by preparing mixtures, computed to be removed just slightly off the boundary so as to avoid the presence of $Ca(OH)_2$, and analyzing the precipitates. Because of this difficulty, the following procedure for determining the composition of the gel coexisting with crystalline $Ca(OH)_2$ at constant concentration of Na_2O was selected as the most expedient and the one likely to give reliable results.

Series of 5 to 10 mixtures each were prepared at Na_2O concentrations (or levels) of 0.2, 2.4, 5.5, 9.2, 11.6, 22.3, 51, 75, and 101 g per liter. (See table 2.) The total quantities of $Ca(OH)_2$ and SiO_2, added as sodium silicate, were estimated from the amounts needed for the solutions as shown in figure 1, plus the approximate amounts required for the precipitates as indicated by results on exploratory

TABLE 2.—*Data pertaining to the* $CaO:SiO_2$ *molar ratios of soda-lime-silicate gels coexisting with* $Ca(OH)_2$ *and solutions containing between 0.19 and 101 g of* Na_2O *per liter*

No.	Composition of mixtures in grams per liter			Age, in weeks	Composition of solutions in grams per liter			Composition of precipitates molar ratios				
									Direct analyses			
	Na_2O	CaO	SiO_2		Na_2O	CaO	SiO_2	Computed $CaO:SiO_2$	Na_2O	CaO	SiO_2	H_2O
1	0.205	1.891	0.655	6	0.195	0.862	0.002	1.69				
2	.200	1.968	.655	18	.190	.888	.002	1.90				
3	.205	1.968	.655	6	.195	.858	.002	1.82				
4	.205	2.042	.655	6	.195	.886	.002	1.90				
5	.205	2.119	.655	6	.195	.912	.003	1.98	0.003	1.94	1.00	3.2
6	.205	2.192	.655	6	.190	.894	.002	2.13				
7	.200	2.270	.655	18	.186	.915	.002	2.23				
8	.200	2.420	.655	18	.188	.911	.002	2.48				
9	[a]2.5	1.058	.655	5	2.37	.193	.003	1.42				
10	2.5	1.135	.655	5	2.38	.237	.003	1.47	.04	1.41	1.00	3.3
11	2.5	1.210	.655	5	2.36	.240	.003	1.59				
12	2.5	1.285	.655	5	2.38	.243	.003	1.71				
13	2.5	1.361	.655	5	2.38	.245	.002	1.83				
14	5.8	0.525	.655	5	5.40	.002	.039	0.92	.18	0.90	1.00	2.60
15	5.8	.600	.655	5	5.42	.010	.015	.99	.15	.98	1.00	2.68
16	5.8	.675	.655	5	5.42	.022	.009	1.08	.13	1.07	1.00	2.80
17	5.8	.750	.655	5	5.42	.041	.005	1.17	.12	1.15	1.00	3.00
18	5.8	.826	.655	5	5.46	.063	.005	1.24	.11	1.21	1.00	3.06
19	5.8	.900	.655	5	5.46	.100	.005	1.32	.07	1.30	1.00	2.98
20	5.8	.975	.655	5	5.46	.099	.003	1.44	.08	1.41	1.00	(3.10)
21	5.8	1.050	.655	5	5.46	.101	.002	1.55	.08	1.52	1.00	(3.35)
22	5.8	1.125	.655	5	5.46	.097	.003	1.69				
23	5.8	1.200	.655	5	5.52	.103	.003	1.80				
24	9.5	0.522	.655	6	9.14	.011	.060	0.92				
25	9.5	.596	.655	6	9.15	.015	.038	1.01				
26	9.5	.671	.655	6	9.17	.025	.017	1.08				
27	9.5	.745	.655	6	9.15	.039	.012	1.18	.14	1.13	1.00	2.9
28	9.5	.820	.655	6	9.14	.046	.007	1.27				
29	9.5	.894	.655	6	9.14	.044	.006	1.40				
30	12.0	.530	.655	5	11.55	.003	.060	0.95				
31	12.0	.606	.655	5	11.53	.007	.025	1.02				
32	12.0	.682	.655	5	11.56	.023	.014	1.05	.19	1.05	1.00	2.7
33	12.0	.757	.655	5	11.56	.036	.008	1.19				
34	12.0	.833	.655	5	11.60	.036	.008	1.315				
35	22.0	.373	.655	5	22.11	.002	.236	0.95				
36	22.0	.466	.655	5	22.11	.003	.149	.98				
37	22.0	.559	.655	5	22.30	.016	.071	1.00	.21	0.94	1.00	2.6
38	22.0	.652	.655	5	22.28	.024	.033	1.08				
39	22.0	.746	.655	5	22.28	.027	.019	1.20				
40	51.0	1.092	1.705	8	50.8	.01	.488	0.95				
41	51.0	1.390	1.705	8	50.9	.01	.178	.97	.22	.95	1.00	2.7
42	51.0	1.688	1.705	8	50.7	.01	.105	1.13				
43	51.0	1.985	1.705	8	50.5	.01	.074	1.30				
44	51.0	2.273	1.705	8	50.5	.01	.070	1.48				
45	75.2	0.993	1.772	4	75.4	.01	.752	1.03				
46	75.2	1.242	1.772	4		.01	.420	0.98				
47	75.2	1.490	1.772	4	75.2	.01	.220	1.03	.24	.95	1.00	2.9
48	75.2	1.737	1.772	4	75.3	.01	.121	1.12				
49	75.2	1.985	1.772	4	75.5	.01	.106	1.28				
50	101.5	0.993	1.772	4	101.2	.01	.721	1.00				
51	101.5	1.242	1.772	4	100.6	.01	.498	1.04	.25	.99	1.00	2.6
52	101.5	1.490	1.772	4	100.8	.01	.320	1.10				
53	101.5	1.737	1.772	4	101.0	.01	.289	1.25				
54	101.5	1.985	1.772	4	100.8	.01	.350	1.49				

[a] The amount of NaO_2 added is approximate in preparations 9 to 54.

mixtures. The $CaO:SiO_2$ ratio was varied systematically in each series so that, after reaction, about half of the mixtures contained $Ca(OH)_2$ and the remainder none. After 4 to 18 weeks the mixtures were filtered and the filtrates analyzed. The computed $CaO:SiO_2$

molar ratios,[2] representing the differences between the amounts of CaO and SiO_2 in the mixtures and the amounts found in solution, are used for the graphical presentation of the data. Most of the precipitates in the series containing 5.4 to 5.5 g of Na_2O per liter were analyzed for check purposes, and in each series those having compositions nearest to the boundary curve were also analyzed. The results are given in table 2.

The $CaO:SiO_2$ molar ratios of the precipitates at the different Na_2O levels are plotted in figure 2 against the amounts of CaO or SiO_2

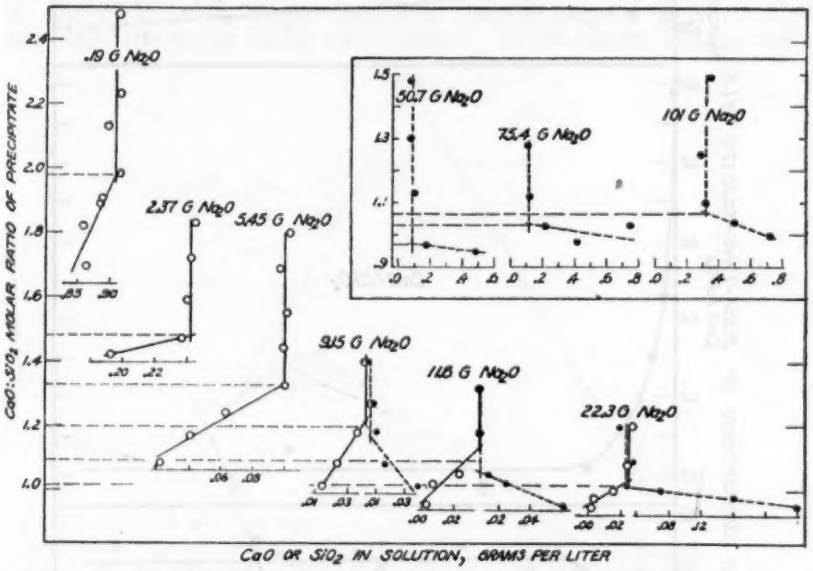

FIGURE 2.—*Plots of the* $CaO:SiO_2$ *molar ratios of precipitates against the amounts of* CaO *or* SiO_2 *in solution for each of nine series of mixtures of varying* CaO *and* SiO_2 *contents but of constant* Na_2O *concentrations.*

O—O=CaO.

●----●=SiO_2.

(or both) in grams per liter of solution. The $CaO:SiO_2$ molar ratios of the gels coexisting with $Ca(OH)_2$ at different Na_2O levels are those corresponding to the "breaks" in the curves shown in figure 2. These breaks were quite sharp except for the series of mixtures containing small amounts of CaO or SiO_2 in solution. This may be due to the experimental errors in the determination of these small quantities and therefore, to obtain as nearly a representative value as possible, the respective concentrations of both constituents were plotted. The average $CaO:SiO_2$ ratio of the two was selected as being more accurate than either one.

The approximate water content of the gels, as moles of H_2O per mole of SiO_2, is given in table 2. However, in table 1 the water content

[2] Both the computed and observed $CaO:SiO_2$ molar ratios were determined, and are given in table 1 for the purpose of indicating the reliability of the former. With a few notable exceptions, in which the observed ratios were markedly lower than the computed ratios, the two agreed within a few hundredths of a mole. Such small differences are not serious, and knowing the cause for the exceptions, the computed ratios only were used in some of the following parts of the study. The marked exceptions, which occurred in the earlier experiments, were due to a partial separation of the solid phases, the $Ca(OH)_2$ adhering firmly to the ceresin lining of the flasks. In subsequent mixtures such separation was prevented by using a finely crystalline $Ca(OH)_2$ and vigorously shaking the mixture during preparation and also at frequent intervals during the first day. The resulting suspensions did not cake in the bottom of the flasks.

of the precipitates showing a $CaO:SiO_2$ molar close to 1 (the precipitates being mostly gel) also indicates approximately the water content of the gels.

The molar ratios of $Na_2O:SiO_2$, $CaO:SiO_2$, and $H_2O:SiO_2$, representing the compositions of the gels along the boundary, $Ca(OH)_2$—soda-lime-silicate gels, are presented graphically in figure 3. This

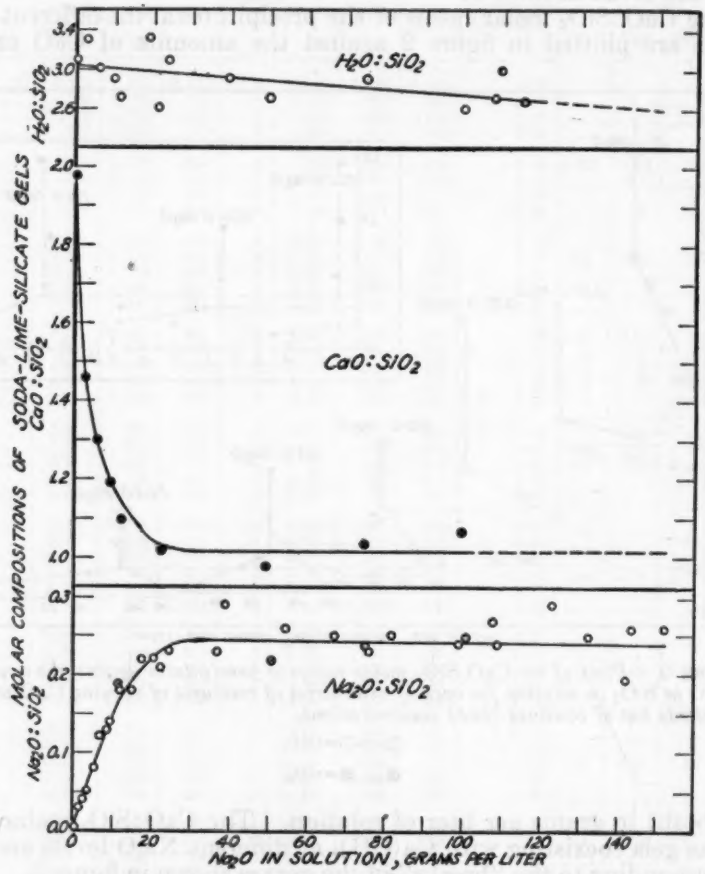

FIGURE 3.—*Relations between the concentrations of* Na_2O *in solution and the compositions of corresponding soda-lime-silicate gels expressed in molar ratios of* $H_2O:SiO_2$, $CaO:SiO_2$, *and* $Na_2O:SiO_2$.

figure, based on data from tables 1 and 2, and figure 2, shows that the $Na_2O:SiO_2$ molar ratio increased from a value of 0.003 to a value of about 0.23 as the concentrations of Na_2O in solution were increased from 0.2 to about 20 g per liter and them remained nearly constant at this value for all higher concentrations of Na_2O, up to 152 g per liter.

The $CaO:SiO_2$ molar ratios of the gels, as shown by figure 2, decreased from 1.98 to 1.00 as the concentration of Na_2O was increased

from 0.2 to 22.3 g per liter. At the higher concentrations of Na_2O used the ratio remained nearly constant at a value of about 1.0.

The H_2O:SiO_2 molar ratios varied between 2.5 and 3.3. This spread in the results is rather large, but not surprising, considering the nature of the materials.

(b) RELATION BETWEEN COMPOSITIONS OF GELS AND SOLUTIONS ALONG BOUNDARY

In order to show the relation between the compositions of the gels and solutions along the boundary, the data for mixtures 5, 10, 19, 27, 32, and 37 in table 2 were computed as mole percent of Na_2O, CaO, and SiO_2, the water being disregarded. These results are plotted in

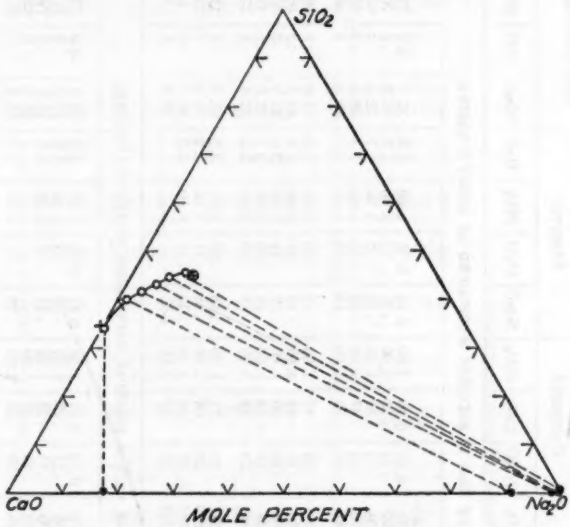

FIGURE 4.—*Compositions of gels coexisting with $Ca(OH)_2$ and of the contact solutions.*

The results are expressed in mole percent of Na_2O, CaO, and SiO_2 (anhydrous basis).

○=Gel.
●=Solution.

THEORETICAL

⊕=$0.25Na_2O.CaO.SiO_2$.
+=$2CaO.SiO_2$.

figure 4. It should be noted that gels and solutions obtained at Na_2O concentrations above 22 g per liter had an average composition, in mole percent, almost identical with that of mixture 37 table 2, and therefore would fall nearly on the same point.

Figure 4 shows that the amounts of SiO_2 in solution along the boundary were relatively small throughout the entire range. It is seen, however, that the decreases in the amounts of CaO in solution caused large changes in the compositions of the gels. But, once the CaO concentrations attained an approximately constant value, the compositions of the gels remained nearly constant.

TABLE 3.—*Data showing the effects of varying concentrations of SiO_2 on the compositions of the soda-lime-silicate gels formed at constant concentrations of Na_2O*

No.	Composition of mixtures			Age	Composition of solutions			Molar composition of precipitates							Composition of solutions (in mole percent)			Composition of precipitates (in mole percent)					
								Computed			Observed							Computed			Observed		
	Na_2O	CaO	SiO_2		Na_2O	CaO	SiO_2	Na_2O	CaO	SiO_2	Na_2O	CaO	SiO_2	H_2O	Na_2O	CaO	SiO_2	Na_2O	CaO	SiO_2	Na_2O	CaO	SiO_2
CONCENTRATION OF Na_2O IN SOLUTION MAINTAINED AT ABOUT 6 G/LITER																							
	g/liter	*g/liter*	*g/liter*	*Weeks*	*g/liter*	*g/liter*	*g/liter*																
1	7.29	1.117	23.43	11	6.61	0.02	17.25	0.11	0.19	1.00	0.15	0.21	1.00	1.5	27.7	0.1	72.3	8.5	14.5	77.0	11.0	15.5	73.5
2	7.02	1.117	19.52	11	6.37	.04	14.92	.14	.25	1.00	.21	.19	1.00	1.8	29.8	.2	70.0	10.0	18.0	72.0	14.5	13.5	71.0
3	6.74	1.117	15.62	11	6.25	.08	12.08	.14	.32	1.00	.21	.25	1.00	1.7	33.9	.4	65.6	9.5	22.0	68.5	14.5	17.0	68.5
4	6.14	1.117	12.16	5	5.66	.05	9.76	.18	.47	1.00	.16	.36	1.00	1.8	36.6	.3	63.1	11.0	28.5	60.5	10.5	23.5	66.0
5	6.47	1.117	11.72	7	6.00	.05	8.82	.16	.39	1.00	.18	.35	1.00	1.9	40.3	.3	59.4	10.5	25.0	64.5	12.0	23.0	65.0
6	6.11	1.117	10.25	5	5.56	.10	7.92	.23	.47	1.00	.18	.38	1.00	1.9	41.0	.7	58.3	11.5	24.5	64.0	11.5	24.5	64.0
7	6.11	1.117	9.62	5	5.59	.03	7.18	.21	.48	1.00	.19	.39	1.00	2.0	43.7	.2	56.1	12.5	28.5	59.0	12.0	24.5	63.5
8	6.10	1.117	8.98	5	5.63	.02	6.61	.19	.50	1.00	.16	.42	1.00	2.0	45.9	.2	53.9	11.5	29.5	59.0	10.0	26.5	63.5
9	6.19	1.117	7.81	11	5.71	.01	5.34	.19	.48	1.00	.18	.50	1.00	2.2	51.6	.1	48.3	11.5	28.5	60.0	10.5	30.0	59.5
10	5.92	1.117	3.91	11	5.56	.01	2.06	.24	.64	1.00	.18	.65	1.00	2.3	72.8	.1	27.0	13.0	34.0	53.0	10.0	35.5	54.5
11	6.03	1.117	2.89	5	5.62	.002	1.21	.24	.71	1.00	.18	.69	1.00	2.5	82.2	.0	17.7	12.5	36.5	51.0	9.5	37.0	53.5
12	5.53	0.746	1.92	5	5.30	.003	0.829	.20	.68	1.00	.18	.71	1.00	2.3	86.5	.0	13.5	10.5	36.0	53.0	9.5	37.5	53.0
13	5.53	.746	1.60	5	5.30	.003	.544	.21	.70	1.00	.19	.73	1.00	2.2	90.7	.0	9.3	11.0	36.5	52.5	10.0	38.0	52.0
14	5.53	.746	1.28	5	5.30	.003	.258	.22	.72	1.00	------	------	------	------	95.4	.0	4.6	11.5	37.0	51.5	------	------	------
CONCENTRATION OF Na_2O IN SOLUTION MAINTAINED AT ABOUT 13 G/LITER																							
15	14.58	1.117	48.86	8	13.57	0.005	40.72	0.12	0.18	1.00	0.17	0.18	1.00	1.6	25.0	0.0	75.0	9.0	14.0	77.0	12.5	13.5	74.0
16	15.85	1.117	43.78	6	14.95	.12	38.56	.17	.20	1.00	.22	.15	1.00	1.6	27.9	.2	71.8	12.5	14.5	73.0	16.0	11.0	73.0
17	14.03	1.117	39.05	8	13.20	.005	34.30	.17	.25	1.00	.18	.23	1.00	1.6	27.8	.0	72.2	12.0	17.5	70.5	13.0	16.0	71.0
18	13.48	1.117	31.23	8	12.72	.005	27.12	.18	.29	1.00	------	------	------	------	31.9	.0	68.1	------	------	------	------	------	------
19	12.94	1.117	23.43	8	12.23	.005	19.68	.18	.32	1.00	.20	.31	1.00	1.9	38.3	.0	61.7	12.0	22.0	68.0	13.0	20.5	66.5
20	15.84	1.117	19.45	8	14.95	.06	17.01	.35	.47	1.00	.22	.39	1.00	1.8	46.7	.2	53.2	19.0	25.5	55.0	14.0	24.0	62.0
21	15.83	1.117	17.02	8	15.05	.02	14.44	.29	.46	1.00	.21	.41	1.00	1.9	51.0	.1	48.9	16.5	26.5	57.0	13.0	25.0	62.0
22	12.38	1.117	15.62	8	11.75	.01	12.72	.21	.41	1.00	.20	.42	1.00	1.9	48.0	.0	52.0	13.0	25.5	61.5	12.5	26.0	62.0
23	15.85	1.117	14.59	8	15.35	.02	12.48	.23	.56	1.00	.21	.46	1.00	1.9	55.1	.1	44.8	13.0	31.0	56.0	12.5	27.5	60.0
24	15.84	1.117	12.16	8	15.40	.02	10.00	.20	.54	1.00	.22	.52	1.00	2.2	60.6	.1	39.3	11.5	31.0	57.5	12.5	30.0	57.5

25	11.83	1.117	7.81	8	11.30	.01	5.52	.23	.52	1.00	.19	.59	1.00	2.1	67.2	.0	32.8	13.0	30.0	57.0	10.5	33.0	56.5
26	11.64	1.117	3.85	5	11.16	.01	2.17	.28	.72	1.00	.21	.65	1.00	2.4	83.8	.0	16.3	14.0	36.0	50.0	11.0	35.0	54.0
27	11.64	0.746	1.92	5	11.25	.01	0.871	.37	.70	1.00	.19	.71	1.00	2.2	92.8	.0	7.2	18.0	34.0	48.0	10.0	37.5	52.5
28	11.64	.746	1.28	5	11.32	.01	.300	.29	.76	1.00	.21	.77	1.00	2.5	97.5	.0	2.5	14.0	37.0	49.0	10.5	39.0	50.5
CONCENTRATION OF Na_2O IN SOLUTION MAINTAINED AT ABOUT 50 G/LITER																							
29	50.0	1.117	158.7	7	48.7	0.00	152.2	(a)	0.18	1.00	0.22	0.09	1.00	1.6	24.2	0.0	75.8	-----	-----	-----	17.0	7.0	76.0
30	50.0	1.117	134.5	7	49.2	.00	126.1	(a)	.14	1.00	.22	.15	1.00	1.8	28.1	.0	71.9	-----	-----	-----	16.0	11.0	73.0
31	50.0	1.117	115.4	7	49.3	.00	106.3	(a)	.13	1.00	.21	.19	1.00	1.9	31.7	.0	68.3	-----	-----	-----	15.0	13.5	71.5
32	50.0	1.117	96.2	7	49.4	.00	91.0	(a)	.22	1.00	.22	.27	1.00	1.8	35.2	.0	64.8	-----	-----	-----	15.0	18.0	67.0
33	50.0	1.117	76.9	7	49.6	.00	70.3	(a)	.18	1.00	.20	.35	1.00	1.9	41.4	.0	58.6	-----	-----	-----	13.0	22.5	64.5
34	50.0	1.117	48.05	7	49.5	.00	42.60	(a)	.21	1.00	.17	.52	1.00	2.2	53.8	.0	46.2	-----	-----	-----	10.0	31.0	59.0
35	50.0	1.117	34.00	5	49.1	.00	31.28	(a)	.43	1.00	.16	.57	1.00	2.0	61.2	.0	38.8	-----	-----	-----	9.0	33.0	58.0
36	50.0	1.117	29.13	5	49.9	.00	25.58	(a)	.34	1.00	.17	.59	1.00	2.3	66.1	.0	33.9	-----	-----	-----	9.5	33.5	57.0
37	50.0	1.117	24.28	5	49.9	.00	22.90	(a)	.86	1.00	.17	.61	1.00	2.2	68.5	.0	31.5	-----	-----	-----	9.5	34.0	56.0
38	50.0	1.117	19.42	5	49.9	.00	17.83	(a)	.74	1.00	.16	.64	1.00	2.2	73.6	.0	26.4	-----	-----	-----	9.0	35.5	55.5
39	50.0	1.117	14.56	5	49.8	.00	13.03	(a)	.77	1.00	.17	.67	1.00	2.4	79.3	.0	20.7	-----	-----	-----	9.0	36.5	54.5
40	50.0	1.117	9.71	5	49.7	.00	8.50	(a)	.98	1.00	.15	.71	1.00	2.2	85.4	.0	14.6	-----	-----	-----	8.0	38.0	54.0
41	50.0	1.117	4.86	5	49.2	.00	3.58	(a)	.93	1.00	.16	.77	1.00	2.3	93.3	.0	6.7	-----	-----	-----	8.5	40.0	52.0
42	50.0	1.117	3.85	5	49.9	.00	2.43	(a)	.97	1.00	.19	.77	1.00	2.7	95.4	.0	4.6	-----	-----	-----	9.5	39.5	51.0
43	50.0	1.117	2.56	5	49.4	.00	1.34	(a)	.97	1.00	.22	.82	1.00	2.8	97.5	.0	2.5	-----	-----	-----	11.0	40.0	49.0
44	50.0	1.117	1.28	5	49.8	.00	0.21	(a)	1.01	1.00	.19	.93	1.00	2.7	99.6	.0	0.4	-----	-----	-----	9.0	44.0	47.0
CONCENTRATION OF Na_2O IN SOLUTION MAINTAINED AT ABOUT 96 G/LITER																							
45	97.0	1.117	76.9	6	-----	-----	-----	(a)	(a)	(a)	0.26	0.49	1.00	2.0	-----	-----	-----	-----	-----	-----	15.0	18.0	67.0
46	97.0	1.117	38.5	6	96.0	0.00	37.17	(a)	(a)	(a)	.23	.63	1.00	2.0	71.0	0.0	29.0	-----	-----	-----	12.0	34.0	54.0
47	97.0	1.117	19.23	6	95.9	.00	18.85	(a)	(a)	(a)	.11	.64	1.00	2.0	83.0	.0	17.0	-----	-----	-----	6.0	37.0	57.0
48	97.0	1.117	9.78	6	95.8	.00	8.76	(a)	(a)	(a)	.17	.82	1.00	1.7	91.0	.0	9.0	-----	-----	-----	8.5	41.0	50.5
49	97.0	1.117	3.92	6	96.1	.00	2.88	(a)	(a)	(a)	.28	.92	1.00	2.7	97.0	.0	3.0	-----	-----	-----	13.0	42.0	45.0

[a] Not computed because of small differences between the amounts in mixtures and those found in solution.

3. REGIONS OF HIGHER SILICA CONCENTRATIONS

The effect of the SiO_2 contents of the solutions on the compositions of the gels was studied by maintaining the concentrations of Na_2O at approximately 6, 13, 50, and 96 g per liter, and increasing the concentrations of SiO_2 in each series to a value of 3.3 moles of SiO_2 per mole of Na_2O. These mixtures contained insufficient $Ca(OH)_2$ to saturate the solutions.

Both the solutions and solids were analyzed and the results are given in table 3. The compositions of the gels were computed only for the 6- and 13-g Na_2O levels, since the computations for the 50- and 96-g Na_2O levels would be subject to large errors due to the relatively small amounts of constituents that precipitated compared to the amounts that remained in solution. The occasional large difference between computed and observed compositions at the 6- and 13-gram Na_2O levels may be due to the same cause.

The last nine columns of table 3 give the compositions of the gels and solutions in mole percentages of Na_2O, CaO, and SiO_2. It may be mentioned that the compositions of the gels computed to mole percent of the four constituents showed that the H_2O content was nearly constant at a value of 55 ± 3 mole percent for all but two of the gels at the different Na_2O levels. It is evident, therefore, that presenting the data for the gels as a ternary system is in reality showing the 55 mole percent H_2O-level of the quaternary system.

The results for the 6-g and 13-g Na_2O levels are plotted in figure 5, and those for the 50- and 96-g Na_2O levels in figure 6. The effect of Na_2O on the compositions of the solids is readily ascertained by comparing the diagrams in the two figures. In order to facilitate the comparison, the amounts of SiO_2 in solution, in grams per liter, are given in the diagrams to the right of the points representing the compositions of the solutions.

Both the computed and observed compositions of the solids are plotted in figure 5. Considering the highly solvated nature of the gels, which made filtration and washing difficult, and that small analytical errors caused large errors in the computed results, the differences between the two sets of values are not to be regarded as significant. The trends of both, however, are about the same, and the averages may be taken as representative of the true compositions of the gels. Figure 5 shows that as the SiO_2 in solution was increased, the mole percent of Na_2O in the gel did not vary greatly, but that of CaO decreased markedly. A comparison of the two diagrams in figure 5 indicates that the gels in contact with solutions of the same mole percent composition have about the same compositions. Noting that a given mole percent of SiO_2 at the two Na_2O levels does not represent the same concentration of SiO_2 in solution, it follows, therefore, that the ratio of SiO_2:Na_2O (or Na_2O:SiO_2), in solution governs greatly the compositions of the gels.

About the same remarks apply to figure 6 as were made for figure 5 except that the curve for the 50-g level, above 65 mole percent of SiO_2 in solution, is displaced slightly further to the right than those at the 6- and 13-g Na_2O levels. Whether this is an actual shift in compositions or is due to an incomplete washing out of the Na_2O and SiO_2 in the solution associated with the gel is not known. The mixtures at the 96-g Na_2O level, having SiO_2 concentrations in excess

of 90 g per liter, contained exceedingly fine-grained precipitates which passed readily through the filter even after 7 weeks of aging and, therefore, only a few filtrates were available for analysis. The few results available at this level do not show as smooth a relation as those at the other levels.

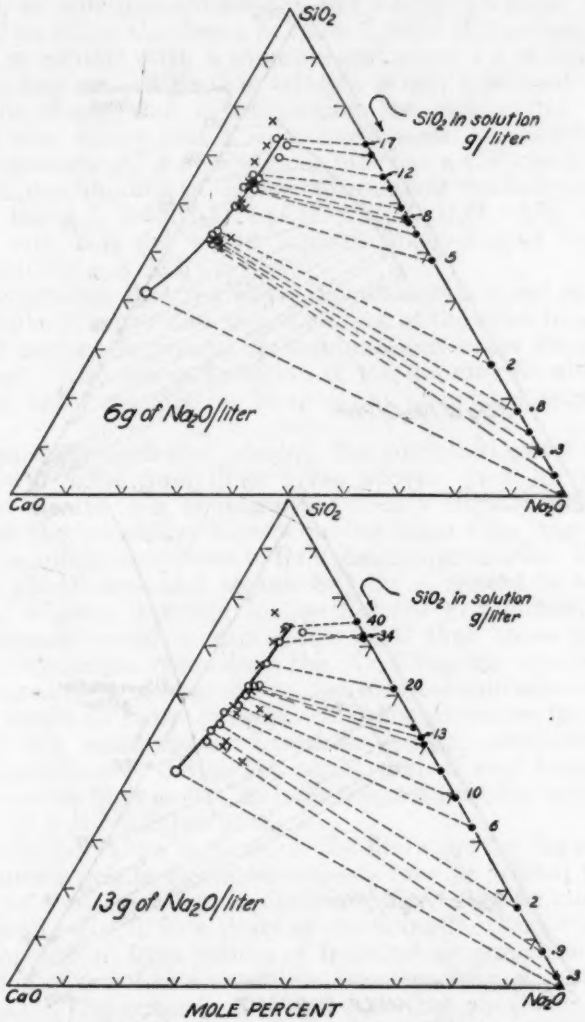

FIGURE 5.—*Compositions of two series of solutions containing 6 and 13 g of* Na_2O *per liter, respectivel,y and of the corresponding gels in mole percent of* Na_2O, CaO *and* SiO_2 *(anhydrous basis).*

○=Gel, analyzed.
×=Gel, computed.
●=Solution, analyzed.

V. APPLICATIONS OF THE RESULTS OF THE STUDY TO CONCRETE

This investigation has shown that gels coexisting with crystalline $Ca(OH)_2$ and with solutions containing between 0.0 and 100 g of

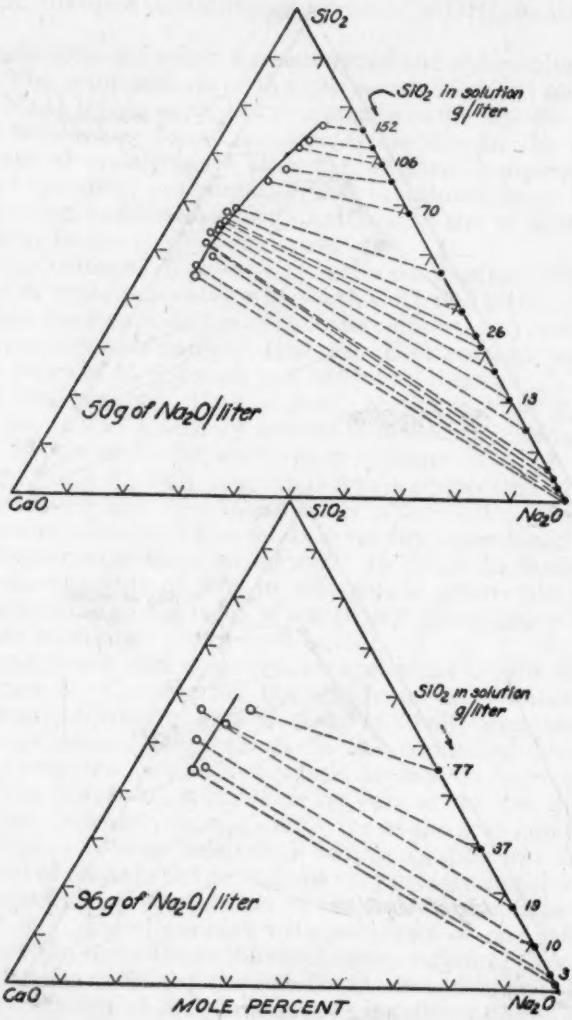

FIGURE 6.—*Compositions of two series of solutions containing 50 and 96 g of* Na_2O *per liter, respectively, and of the corresponding gels in mole percent of* Na_2O, CaO, *and* SiO_2 *(anhydrous basis).*

○=Gel.
●=Solution.

Na_2O per liter have compositions that range between about $2CaO.1SiO_2.xH_2O$ and $0.25Na_2O.1CaO.1SiO_2.xH_2O$. If similar relations prevail in a completely hydrated cement, the approximate compositions of the gel and solution may be deduced as follows:

For purposes of illustration, a cement containing 20 percent of SiO_2 and 1 percent of Na_2O is used. The extent of combination of Na_2O and SiO_2 as a soda-lime-silicate gel will depend on the extent to which the Na_2O-bearing compounds and the two lime silicates have hydrolyzed. Because of this the simplest deductions, as follows, are those for a completely hydrated cement. If all of the Na_2O combined with SiO_2 as soda-lime-silicate gel, the Na_2O:SiO_2 molar ratio of the gel would be 0.05. As shown in figure 3, a gel of this Na_2O:SiO_2 ratio is stable in contact with a solution containing 3 g of Na_2O per liter. Since this amount [3] of Na_2O in solution is only 2 percent of the total, it may be disregarded in calculating the composition of the gel. Figure 3 also shows that a soda-lime-silicate gel coexisting with a solution containing 3 g of Na_2O per liter has a CaO:SiO_2 molar ratio of 1.4. A combination of the two ratios gives the following composition for the gel, $0.05Na_2O:1.4CaO:1SiO_2:xH_2O$. The solution in contact with this gel would contain about 3 g of Na_2O, 0.1 g of CaO, and 0.005 g of SiO_2 per liter.

It is recognized that the above calculations are not entirely valid. For example, it is probable that a portion of the silica in a completely hydrated cement is present in combinations other than soda-lime-silicate gel. Also the composition of the gel may be altered by the prolonged aging required to bring about complete hydration of the cement.

In a partially hydrated cement, the compositions of the gel and solution will differ from those given above. It is known that the dicalcium silicate in a cement paste is only slightly hydrated at 28 days, but the tricalcium silicate in the same time may approach a state of complete conversion to its hydration products. Since, on the average, about one-third of the SiO_2 in a cement is combined as dicalcium silicate, it would follow that the gels formed during the earlier periods would contain more Na_2O than those prevailing at complete hydration, providing the Na_2O-bearing compounds react with water at rates comparable to that of tricalcium silicate. Also the solution would be richer in soda. Making allowance for the average value of SiO_2 combined as dicalcium silicate, calculations indicate that the gels formed during the earlier periods may have Na_2O:SiO_2 molar ratios as high as 0.1, and the contact solution may contain as much as 10 g of Na_2O per liter.

The different values reported in the literature for the compositions of the silicate gels in hydrated cements may be related to the alkali contents of the cements as indicated by the following considerations. Bogue and Lerch [2], in a study of the alkali-free lime silicates, came to the conclusion, from results of free-lime determinations, that the hydrated products had compositions approaching a value of $2CaO:SiO_2:xH_2O$. This result is in accord with that obtained in studies of the system line-silica-water reported by Flint and Wells [3] and Bessey [4]. Using cements that contained between 0.6 and 1.5 percent of total alkalies, Bessey [5] concluded from calorimetric results and free-lime determinations that the hydrous silicates formed in the pastes had a composition of about $3CaO:2SiO_2:xH_2O$. This value of the CaO:SiO_2 ratio is in fair agreement with that computed

[3] In making these computations, the C/W ratio was selected as 2.86 by weight, and it was assumed that the "fixed" water amounted to 30 percent by weight of the cement. No allowance was made for water gained or lost by the paste.

in this study for hydrated cements containing about 1 percent of Na_2O.

Concretes made from high-alkali cements and aggregates containing opal or certain other active siliceous materials have been shown by numerous investigations to be unsound. A gelatinous product formed in such concrete is generally associated with this unsound state. Analyses of some of these gels show them (see table 4) to consist largely of silica, alkalies, and water (ignition loss), together with

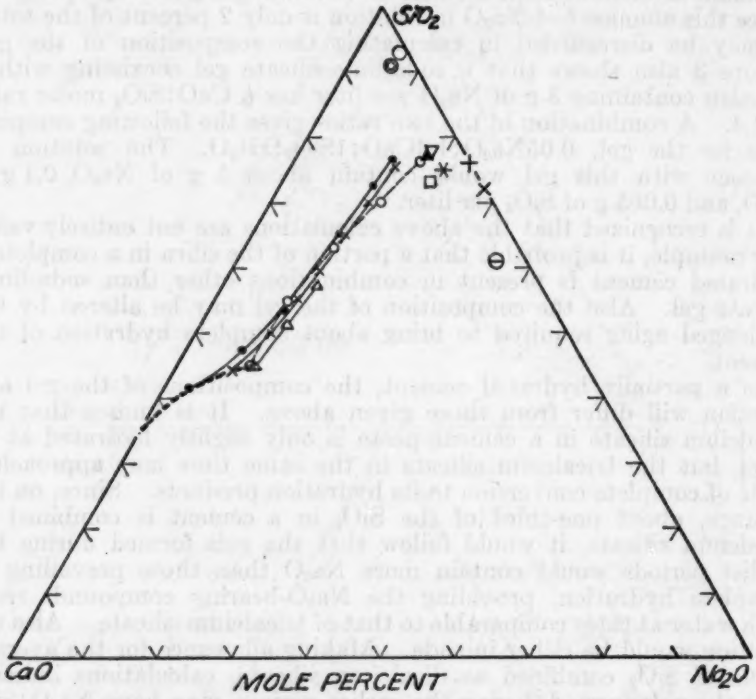

FIGURE 7.—*Compositions of synthetic gels and of gels found in concretes showing expansion and cracking*

The results are expressed in mole percent of Na_2O, CaO, and SiO_2 (anhydrous basis).

●—● Composition of gels, solution containing 6 g of Na_2O/liter.
×—× Composition of gels, solution containing 13 g of Na_2O/liter.
○—○ Composition of gels, solution containing 50 g of Na_2O/liter.
△—△ Composition of gels, solution containing 96 g of Na_2O/liter.
--- Composition of gels coexisting with Ca (OH)$_2$

COMPOSITION OF GELS FROM CONCRETE

○=Meissner.
◎=Coombs.
▲=Stanton.
▽=Stanton.
□=Meissner.
×=Blanks.
+=Meissner.
⊖=Hanna.
*=Average of above.

smaller quantities of CaO, R_2O_3, MgO, and SO_3. The data computed to mole percent of Na_2O (the K_2O being counted as Na_2O), CaO, and SiO_2 are presented in figure 7. Since some of the constituents were disregarded in these computations, the results are to be considered as only approximating the true ratio of Na_2O to CaO to SiO_2 of the gels. Giving consideration to this and the fact that the gels were

obtained from different sources under different circumstances, the spread in the data is not surprising. The average of these compositions is given in figure 7 for facilitating comparisons between the synthetic gels and those found in concrete. The compositions of the gels shown in figure 7 are those previously given in figures 4, 5, and 6.

TABLE 4.—*Percentage oxide compositions of gels found in or on concretes containing "reactive" aggregates*

Number	SiO_2	R_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	Loss	Reported by—
1	81.9	0.7	1.1	-------	-------	4.0	2.0	10.5	Meissner [6]
2[a]	85.0	2.2	2.0	-------	-------	4.4	1.9	16.1	Coombs [7]
3	53.4	7.8	2.6	0.8	-------	12.8	[b]	[c] 16.7	Stanton [8]
4[d]	53.9	6.8	2.9	.6	-------	12.9	[b]	[c] 22.4	Do.
5	53.4	1.5	4.7	.0	0	12.7	4.5	20.5	Meissner [6]
6	58.7	.5	0	.0	0	19.9	6.5	13.8	Blanks [9]
7	51.2	-------	-------	-------	0	16.8	[b]	-------	Meissner [6]
8	50.0	.5	2.8	.2	2.6	24.7	8.2	11.0	Hanna [9]

[a] Analysis of water soluble portion of gel amounting to 90.9 percent of total (ignited basis)— loss on ignition determined on gel as found.
[b] K_2O counted with Na_2O.
[c] Sum of "Moisture" and "Combined H_2O and organic matter."
[d] Analyses also show 3.9 percent of CO_2 and 0.5 percent of Cl.

Because large amounts of $Ca(OH)_2$ are present in concrete, it might seem that the compositions given in table 4 should approximate those of the gels which coexist with $Ca(OH)_2$, as determined in this study. An examination of figure 7, however, shows that the reported compositions of the gels in concrete are notably and consistently lower in CaO and either higher or lower in Na_2O than those along the boundary.

A theory advanced recently by Hansen [10] to account for expansion of concretes containing "reactive" aggregates and alkalies also appears to explain why such low-lime alkali silicates may be present in concrete. This theory postulates that a membrane, permeable to sodium and hydroxyl ions and water but impermeable to silicate ions, is formed around the "reactive" aggregate particles. As a result of the transfer of the alkali hydroxide solution, an osmotic pressure great enough to cause expansion is produced. Also there occurs a reaction between the alkali hydroxide and the siliceous aggregate forming alkali silicates.

VI. SUMMARY

The only solids found, in the foregoing study of portions of the system soda-lime-silica water at 25° C, were $Ca(OH)_2$ and a four-component gelatinous product of variable composition. In contact with crystalline $Ca(OH)_2$ and solutions of increasing Na_2O contents, this gel showed a composition varying between $0.003\ Na_2O:2.0\ CaO:1.0SiO_2:xH_2O$ (at 0.2 g of Na_2O per liter) and $0.25Na_2O:1.0\ CaO:1.0SiO_2:xH_2O$ (at 20 to 101 g of Na_2O per liter). By increasing the concentrations of SiO_2 in solution, at fixed Na_2O levels (6, 13, 50, and 96 g per liter), the $Na2O:SiO_2$ molar ratio of the gel was shown to increase to a value of about 0.2 and remain approximately constant at this value. The $CaO:SiO_2$ molar ratio, however, decreased at all Na_2O levels.

The compositions of gels from concrete containing "reactive" aggregates are compared with those of the synthetic gels.

It is shown that the low-lime gels formed in concrete approximate in composition those in the study in contact with solutions the SiO_2: Na_2O ratio of which approaches a value of 3.

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WASHINGTON, April 4, 1944.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1591

Part of Journal of Research of the National Bureau of Standards, Volume 32, June 1944

LAMINAR FLOW AT THE INTERFACE OF TWO LIQUIDS

By Garbis H. Keulegan

ABSTRACT

The velocity distribution in the laminar boundary layers at the interface of two liquids in relative rectilinear motion, the thickness of the layers, and the stress at the interface are determined. Numerical results are given for nine cases of liquids in contact, including identical liquids and liquids with varying degrees of dissimilarity in characteristics. The evaluation of the desired quantities is based on Prandtl's boundary-layer theory, and is carried out by a method of successive approximations. The numerical results are those given by the second approximation.

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I. INTRODUCTION

When a liquid of given density is flowing over a liquid of greater density, the latter being at rest, three successive forms of the interface are discernible as the velocity of the moving liquid is increased. To take a concrete example, let us assume that the flow takes place in a closed rectangular channel with a lower pool; the upper liquid is fresh water and the lower liquid is a solution of salt or sugar in water. First, at small velocities, the surface of separation is sharp and distinct, indicating, since the indices of refraction of the liquids are different, that the densities are discontinuous at the interface and the flow at the interface is laminar. The flow in the central part of the upper liquid, on the other hand, may be laminar or turbulent, depending on the size of the channel. Secondly, if the velocity of the upper liquid is gradually increased, at some critical velocity the smoothness of the separating surface first disappears, and then the surface becomes covered with surface waves traveling in the direction of the current and with a velocity slightly smaller than the velocity of the upper current. When the waves first appear, they are long-

crested, that is, the length of the crests normal to the direction of motion is greater than the spacing between the crests. The crest lines are parabolic, concave upstream, and highest at the center of the channel, but flattening out toward the channel wall. At this stage of the flow—and this perhaps is significant—the waves are stable and show no tendency to break. The waves travel with practically no deformation, except the tendency to grow slightly larger during their motion. Finally, when the velocity of the upper current exceeds the critical velocity, the waves become sharp-crested and the crests shorter. The waves no longer are stable; that is, portions of the crests break away from the waves and are thrown into the upper current. These portions move forward and upward. In fact, this is the manner by which the mixing of the lower liquid with the moving liquid is brought about. When the velocity of the current is increased, still further within certain limits, the rate of mixing increases. At this stage of the flow, and this also is perhaps significant, the wave length is not affected by changes of velocity. These are the main results of observations made in a laboratory channel where the depth of the upper current is not over 10 centimeters and the length of the channel is not over 10 meters.

A detailed explanation of these phenomena is lacking. A theoretical approach supplementing experimental knowledge should prove helpful. A theoretical investigation should begin with a study of the stability of the interface on the basis of the actual conditions in the neighborhood of the interface. One of these conditions is a discontinuity of density at the surface of separation. Another is a pair of laminar boundary layers on the two sides of the surface of separation. In this paper the thicknesses of these boundary layers and the velocity distributions within them are determined by means of successive approximations, on the assumption that the interface is a smooth, plane surface.

II. FORMULATION OF THE PROBLEM

A liquid of indefinite height and having initially a uniform velocity, U, meets and flows over a still liquid of indefinite depth. In general, the two liquids have different physical characteristics; that is, their viscosities and densities are not the same. It will be assumed that the lower liquid has the greater density. If the pressure is everywhere hydrostatic, the interface or surface of separation is a horizontal plane. When U is sufficiently small the narrow region on both sides of the interface is a region of viscous laminar flow. Thus, the activating forces at the point where the moving liquid comes first in contact with the lower liquid are tangential and act in the horizontal direction; there is no normal force acting on the interface and hence the interface remains horizontal. Every particle of liquid on the interface moves with a constant velocity, u_0. The thickness of the viscous boundary layers in the two liquids is initially zero and increases with the length downstream (see fig. 1). In the upper layer the velocity in a vertical section increases from u_0 to U; in the lower layer it decreases from u_0 to 0. It is proposed to evaluate the variation of the thickness of the laminar layer with the length of the interface, the variation of velocity in the two layers, the shearing stress at the interface and the dependence of these quantities on the physical characteristics of the two liquids.

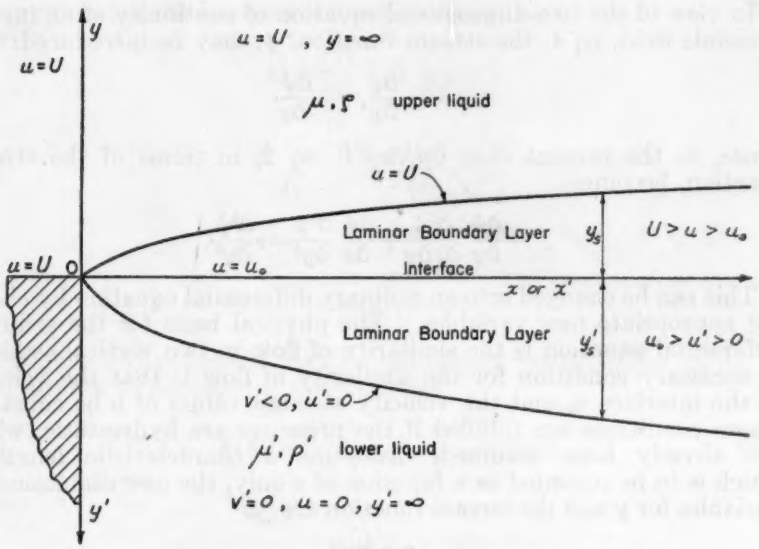

FIGURE 1.—*Laminar boundary layers at the interface of two liquids.*

III. PRANDTL'S BOUNDARY-LAYER EQUATION

In order to avoid negative values of ordinates two distinct sets of axes will be used, x, y for the upper liquid and x', y' for the lower liquid. See figure 1. The x-axes of the two sets coincide and lie in the plane of separation of the two liquids, the positive sense being in the direction of U. The point at which the two liquids first come into contact will be taken as the origin. In the upper liquid, positive y is directed upward; in the lower liquid, positive y' is directed downward. The density, the viscosity, and the kinematic viscosity of the upper liquid will be denoted by ρ, μ and ν, respectively, and the corresponding properties of the lower liquid by ρ', μ', and ν', respectively. The parameter, r, defined as

$$r=\sqrt{[\mu'\rho'/\mu\rho]}, \tag{1}$$

is of special significance in this analysis, as will be seen subsequently.

The basis of these computations is the boundary-layer equation of Prandtl for the two-dimensional flow of an incompressible fluid [1].[1] This equation with the law of hydrostatic pressure and the equation of continuity, when expressed in terms of the upper liquid, becomes

$$u\frac{\partial u}{\partial x}+v\frac{\partial u}{\partial y}=\nu\frac{\partial^2 u}{\partial y^2}-\frac{1}{\rho}\frac{\partial p}{\partial x}, \tag{2}$$

$$\frac{1}{\rho}\frac{\partial p}{\partial y}+g=0, \tag{3}$$

$$\frac{\partial u}{\partial x}+\frac{\partial v}{\partial y}=0, \tag{4}$$

where u and v are the components of velocity in the x and y directions, respectively, and p is the hydrostatic pressure.

[1] The figures in brackets indicate the literature references at the end of this paper.

In view of the two-dimensional equation of continuity of an incompressible fluid, eq 4, the stream function, ψ, may be introduced:

$$u=-\frac{\partial\psi}{\partial y},\ v=\frac{\partial\psi}{\partial x}. \tag{5}$$

Since, in the present case $\partial p/\partial x=0$, eq 2, in terms of the stream function, becomes

$$-\frac{\partial\psi}{\partial y}\frac{\partial^2\psi}{\partial x\partial y}+\frac{\partial\psi}{\partial x}\frac{\partial^2\psi}{\partial y^2}=\nu\frac{\partial^3\psi}{\partial y^3}. \tag{6}$$

This can be changed into an ordinary differential equation by choosing appropriate new variables. The physical basis for the ordinary differential equation is the similarity of flow in two vertical sections. A necessary condition for the similarity of flow is that the velocity at the interface u_0 and the velocity at large values of y be constant. These conditions are fulfilled if the pressures are hydrostatic, which has already been assumed. Adopting a characteristic length δ, which is to be regarded as a function of x only, the new dimensionless variables for y and the stream function are

$$\eta=ny/\delta, \tag{7}$$

and

$$H(\eta)=-\psi/U\delta, \tag{8}$$

where n is a dimensionless numerical constant as yet not specified. These variables are dimensionless. In terms of these, eq 6 now becomes

$$U\frac{d\delta}{dx}H\frac{d^2H}{d\eta^2}+n\frac{\nu}{\delta}\frac{d^3H}{d\eta^3}=0. \tag{9}$$

Thus, if we select δ to satisfy the relation

$$\delta\frac{d\delta}{dx}=n\frac{\nu}{U},$$

or

$$\delta^2=2n\frac{\nu x}{U}, \tag{10}$$

then, from eq 9, we have

$$\frac{d^3H}{d\eta^3}+H\frac{d^2H}{d\eta^2}=0, \tag{11}$$

which is Blasius' equation for the laminar boundary layer when the pressure is independent of x [2].

In eq 10 the dependence of δ on x is given except for the numerical value of n. We determine this by considering the velocity at large values of y. Now,

$$u=-\frac{\partial\psi}{\partial y}=nU\frac{dH}{d\eta},$$

hence if we specify that $dH/d\eta=1$ for large values of η, and this is a boundary condition for the upper fluid, we must then take $n=1$. These values we now adopt.

Summarizing, we have for the upper liquid

$$L(\eta)=\frac{d^3H}{d\eta^3}+H\frac{d^2H}{d\eta^2}=0, \tag{12}$$

where

$$H=-\frac{\psi}{U\delta},\ \eta=\frac{y}{\delta}, \tag{13}$$

and

$$\delta=\sqrt{\frac{2\nu x}{U}}. \tag{14}$$

A similar set of equations may be established for the lower liquid by using primes to distinguish the variables,

$$L(\eta')=\frac{d^3H'}{d\eta'^3}+H'\frac{d^2H'}{d\eta'^2}=0, \tag{15}$$

where

$$H'=-\frac{\psi'}{U\delta'},\ \eta'=\frac{y'}{\delta'}, \tag{16}$$

and

$$\delta'=\sqrt{\frac{2\nu' x}{U}}. \tag{17}$$

The actual velocities and their first derivatives in terms of the dimensionless variables are

$$u=U\frac{dH}{d\eta}, \tag{18}$$

$$\frac{\partial u}{\partial y}=\frac{U}{\delta}\frac{d^2H}{d\eta^2}, \tag{19}$$

for the upper liquid; and

$$u'=U\frac{dH'}{d\eta'}, \tag{20}$$

$$\frac{\partial u'}{\partial y'}=\frac{U}{\delta'}\frac{d^2H'}{d\eta'^2}, \tag{21}$$

for the lower liquid.

For the simultaneous solution of the two basic differential equations, eq 12 and 15, six boundary conditions are needed. These we now consider. In the upper liquid, u equals U for $y=\infty$; in the lower liquid, u' vanishes for $y'=\infty$. Accordingly,

$$\frac{dH}{d\eta}=1,\ \eta=\infty; \tag{22}$$

and

$$\frac{dH'}{d\eta'}=0,\ \eta'=\infty. \tag{23}$$

The stream function, ψ, may be interpreted as the flux per unit width between a point y of the upper liquid and the interface; and ψ' as the flux per unit width between a point y' of the lower liquid and the interface. As we have supposed that the interface is the horizontal plane $y=y'=0$, we must have

$$H=0,\ \eta=0; \tag{24}$$

and

$$H'=0,\ \eta'=0. \tag{25}$$

The velocities are continuous at the interface; hence

$$\frac{dH}{d\eta}=\frac{dH'}{d\eta'},\ \eta=\eta'=0. \tag{26}$$

Again, the shearing forces are continuous at the interface; hence

$$\mu\frac{\partial u}{\partial y}=-\mu'\frac{\partial u'}{\partial y'},\ y=y'=0,$$

$$\frac{\mu}{\sqrt{\nu}}\frac{d^2H}{d\eta^2}=-\frac{\mu'}{\sqrt{\nu'}}\frac{d^2H'}{d\eta'^2},\ \eta=\eta'=0,$$

or, using eq 1,

$$\frac{d^2H}{d\eta^2}=-r\frac{d^2H'}{d\eta'^2},\ \eta=\eta'=0. \tag{27}$$

These are the six boundary conditions of the problem.

IV. APPROXIMATE EXPRESSIONS FOR THE STREAM FUNCTIONS

To solve the differential equations, eq 12 and 15, we shall resort to a method of approximations which is a modification of the method used by Pohlhausen for the solution of the Blasius plate problem [3].

In this method certain approximate boundary conditions for large values of η and η' are required. First, consider the upper moving liquid. Select the value η_s of η such that

$$1-\frac{dH}{d\eta}\leqq\epsilon,\ \text{if}\ \eta\geqq\eta_s, \tag{28}$$

where ϵ is a small quantity, say 1/100 or any other smaller fraction. Denote the value of H corresponding to η_s by H_s. Now, writing eq 12 in the form

$$\frac{d^2H}{d\eta^2}=-\frac{1}{H}\frac{d^3H}{d\eta^3}, \tag{29}$$

and integrating between $\eta=\eta_s$ and $\eta=\infty$, we have

$$1-\left(\frac{dH}{d\eta}\right)_{\eta_s}=-\int_{\eta_s}^{\infty}\frac{1}{H}\frac{d^3H}{d\eta^3}\,d\eta.$$

Integrating the right-hand member by parts, and neglecting the term multiplied by ϵ, and making an obvious substitution from eq 29, using eq 28, we obtain

$$1-\left(\frac{dH}{d\eta}\right)_{\eta_s}=\frac{1}{H_s}\left(\frac{d^2H}{d\eta^2}\right)_{\eta_s}+\int_{\eta_s}^{\infty}\frac{1}{H^3}\frac{d^3H}{d\eta^3}\,d\eta.$$

Treating the integral in the right-hand member again in the same manner, we obtain

$$1-\left(\frac{dH}{d\eta}\right)_{\eta_s}=\left(\frac{d^2H}{d\eta^2}\right)_{\eta_s}\left(\frac{1}{H_s}-\frac{1}{H_s^3}\right)-3\int_{\eta_s}^{\infty}\frac{1}{H^5}\frac{d^2H}{d\eta^3}\,d\eta.$$

If ϵ is sufficiently small, that is, if H_s is sufficiently large, the integral in the latter equation may be discarded, leaving

$$1-\left(\frac{dH}{d\eta}\right)_{\eta_s}=\left(\frac{d^2H}{d\eta^2}\right)_{\eta_s}\left(\frac{1}{H_s}-\frac{1}{H_s^3}\right). \tag{30}$$

This is the approximate relation which exists between the first and second derivatives of H when $\eta=\eta_s$.

If we now suppose that H_s is so large that 1 can be neglected compared to the square of H_s, then, in view of eq 28, 29, and 30, we must have

$$\left.\begin{aligned}\frac{dH}{d\eta}&=1-\epsilon, && \eta=\eta_s,\\ \frac{d^2H}{d\eta^2}&=\epsilon H_s, && \eta=\eta_s,\\ \frac{d^3H}{d\eta^3}&=-\epsilon H_s^2, && \eta=\eta_s.\end{aligned}\right\} \tag{31}$$

Consider now the lower still liquid. We select the value η_s' of η', such that

$$\frac{dH'}{d\eta'}\leqq\epsilon', \text{ if } \eta'\geqq\eta_s', \tag{32}$$

where ϵ' has the same general meaning as ϵ. Denote the value of H' corresponding to η_s' by H_s'. For values of η' larger than η_s', eq 15 may be written in the form

$$\frac{d^3H'}{d\eta'^3}=-H_s'\frac{d^2H'}{d\eta'^2}.$$

Obviously, then

$$\left.\begin{aligned}\frac{dH'}{d\eta'}&=\epsilon', && \eta'=\eta_s',\\ \frac{d^2H'}{d\eta'^2}&=-\epsilon'H_s', && \eta'=\eta_s',\\ \frac{d^3H'}{d\eta'^3}&=\epsilon'H_s'^2, && \eta'=\eta_s'.\end{aligned}\right\} \tag{33}$$

Now, in the method employed here, the end conditions for the large values of η and η' will be taken from eq 31 and 33 after assigning definite values to ϵ and ϵ'. The values assigned to ϵ and ϵ' have a bearing on the accuracy of the approximation and also govern the course of the computations. If ϵ and ϵ' are assigned values different from zero, the accuracy of the approximation is increased, but the analysis becomes more complicated. In order to simplify computations, we

shall take $\epsilon=\epsilon'=0$ and adopt the following end conditions. For the upper liquid, we have

$$\frac{dH}{d\eta}=1,\ \frac{d^2H}{d\eta^2}=0,\ \frac{d^3H}{d\eta^3}=0,\ \eta=\eta_s, \tag{34}$$

and for the lower liquid,

$$\frac{dH'}{d\eta'}=0,\ \frac{d^2H'}{d\eta'^2}=0,\ \frac{d^3H'}{d\eta'^3}=0,\ \eta'=\eta_s'. \tag{35}$$

These now replace the conditions implied by eq 22 and 23. With this choice of the end conditions, η_s and η_s' have simple geometric interpretations. Let y_s and y_s' be the values of the distance from the interface corresponding to η_s and η_s', respectively; that is, let

$$y_s=\eta_s\sqrt{(2\nu x/U)}, \tag{36}$$

and

$$y_s'=\eta_s'\sqrt{(2\nu' x/U)}, \tag{37}$$

then y_s and y_s' are the thicknesses of the two laminar boundary layers at the interface.

We shall also need the following end conditions from eq 24, 25, 26, for the upper liquid,

$$H=0,\ \frac{dH}{d\eta}=a_0,\ \eta=0, \tag{38}$$

and for the lower liquid,

$$H'=0,\ \frac{dH'}{d\eta'}=a_0',\ \eta'=0, \tag{39}$$

where

$$a_0=a_0'=u_0/U.$$

We are now ready to develop the general expressions for the stream functions H and H'. Since from eq 15 and 34, $d^3H/d\eta^3$ vanishes at $\eta=0$ and $\eta=\eta_s$, then it must be possible to express this function of H as a summation of polynomials where each polynomial vanishes for $\eta=0$ and $\eta=\eta_s$. Suitable polynomials may be selected in various ways. In order to extend Pohlhausen's computations [3], we select the following oscillating algebraic functions as the expansion polynomials for this analysis:

$$N_1=-\alpha(\alpha-1)=\alpha-\alpha^2,$$

$$N_2=+\alpha(\alpha-1)(2\alpha-1)=2\alpha^3-3\alpha^2+\alpha,$$

$$N_3=-\alpha(\alpha-1)(3\alpha-1)(3\alpha-2)=2\alpha-11\alpha^2+18\alpha-9\alpha^4,$$

and, in general,

$$N_n=(-1)^n\alpha(\alpha-1)(n\alpha-1)(n\alpha-2)(n\alpha-3)(\ \ldots\ )(n\alpha-n+1),$$

where

$$\alpha=\eta/\eta_s.$$

Using only the first three functions, we put

$$\frac{dH^3}{d\eta^3}=\frac{a_1}{\eta_s}(-6N_1+32k_2N_2-30k_3N_3). \tag{40}$$

Here a_1, η_s, k_2, and k_3 are constants to be determined. Integrating once with respect to η, we have

$$\frac{d^2H}{d\eta^2}=a_1(J_1+k_2J_2+k_3J_3), \tag{41}$$

where J_1, J_2 and J_3 are functions of α:

$$J_1=1-3\alpha^2+2\alpha^3,$$

$$J_2=16\alpha^2-32\alpha^3+16\alpha^4,$$

$$J_3=1-30\alpha^2+110\alpha^3-135\alpha^4+54\alpha^5.$$

It must be remarked that J_1 is derived from N_1 by integrating with respect to η and selecting the constant of integration so that $J_1=0$ for $\alpha=1$, and similarly for J_2 and J_3. Equation 41 thus obviously satisfies the second end conditions in eq 34. Integrating eq 41 with respect to η, we have

$$\frac{dH}{d\eta}=a_0+a_1\eta_s(G_1+k_2G_2+k_3G_3), \tag{42}$$

where G_1, G_2, and G_3 are functions of α:

$$G_1=\alpha-\alpha^3+\frac{1}{2}\alpha^4,$$

$$G_2=\frac{16}{3}\alpha^3-8\alpha^4+\frac{16}{5}\alpha^5,$$

$$G_3=\alpha-10\alpha^3+\frac{55}{2}\alpha^4-27\alpha^5+9\alpha^6.$$

In this case, G_1 is derived from J_1 by integrating the latter with respect to η and selecting the constant of integration so that $G_1=0$ when $\eta=0$, and similarly for G_2 and G_3. The constant a_0 is introduced in order to satisfy the second end conditions in eq 38. Integrating eq 42 with respect to η, we have

$$H=a_0\eta_sF_0+a_1\eta_s^2(F_1+k_2F_2+k_3F_3), \tag{43}$$

where F_0, F_1, F_2, and F_3 are functions of α:

$$F_0=\alpha,$$

$$F_1=\frac{1}{2}\alpha-\frac{1}{4}\alpha^4+\frac{1}{10}\alpha^5,$$

$$F_2=\frac{4}{3}\alpha^4-\frac{8}{5}\alpha^5+\frac{8}{15}\alpha^6,$$

$$F_3=\frac{1}{2}\alpha^2-\frac{5}{2}\alpha^4+\frac{11}{12}\alpha^5-\frac{9}{2}\alpha^6+\frac{9}{7}\alpha^7,$$

where F_1 is derived from G_1 by integrating the latter with respect to η and selecting the constant of integration so that $F_1=0$ when $\eta=0$, and similarly for F_0, F_2, and F_3. It is obvious that the first of the end conditions in eq 38 is satisfied. The functions N, J, G, and F are tabulated in tables 1, 2, 3, and 4.

TABLE 1.—*Values of the N functions*

α	$N_1(\alpha)$	$N_2(\alpha)\times 10$	$N_3(\alpha)\times 10$
0.00	0.0000	0.0000	0.0000
.05	.0475	.4275	.7030
.10	.0900	.7200	1.0710
.15	.1275	.0925	1.0869
.20	.1600	.9600	0.8960
.25	.1875	.9375	.5859
.30	.2100	.8400	.2310
.35	.2275	.6825	−.1081
.40	.2400	.4800	−.3840
.45	.2475	.2475	−.5631
.50	.2500	−.0000	−.6250
.55	.2475	−.2475	−.5631
.60	.2400	−.4800	−.3840
.65	.2275	−.6825	−.1081
.70	.2100	−.8400	.2310
.75	.1875	−.9375	.5859
.80	.1600	−.9600	.8960
.85	.1275	−.8925	1.0869
.90	.0900	−.7200	1.0710
.95	.0475	−.4275	0.7030
1.00	.0000	−.0000	.0000

TABLE 2.—*Values of the J functions*

α	$J_1(\alpha)$	$J_2(\alpha)$	$J_3(\alpha)$
0.00	1.0000	0.0000	1.0000
.05	0.9929	.0344	0.9451
.10	.9720	.1296	.7971
.15	.9393	.2632	.6312
.20	.8960	.4096	.4842
.25	.8437	.5624	.3690
.30	.7840	.7056	.3075
.35	.7183	.8280	.2979
.40	.6480	.9216	.3366
.45	.5747	.9800	.4105
.50	.5000	1.0000	.5001
.55	.4253	0.9800	.5904
.60	.3520	.9216	.6633
.65	.2817	.8280	.7008
.70	.2160	.7056	.6942
.75	.1563	.5624	.6309
.80	.1040	.4096	.5280
.85	.0607	.2632	.3675
.90	.0280	.1296	.2037
.95	.0073	.0344	.0615
1.00	.0000	.0000	.0000

TABLE 3.—*Values of the G functions*

α	$G_1(\alpha)$	$G_2(\alpha)$	$G_3(\alpha)$
0.00	0.0000	0.0000	0.0000
.05	.0499	.0011	.0480
.10	.0990	.0045	.0927
.15	.1469	.0144	.1270
.20	.1928	.0299	.1569
.25	.2363	.0552	.1760
.30	.2770	.0869	.1942
.35	.3146	.1254	.2093
.40	.3488	.1691	.2255
.45	.3793	.2168	.2444
.50	.4062	.2669	.2641
.55	.4294	.3165	.2932
.60	.4488	.3640	.3244
.65	.4646	.4077	.3590
.70	.4771	.4464	.3937
.75	.4863	.4781	.4272
.80	.4928	.5024	.4559
.85	.4969	.5191	.4783
.90	.4990	.5288	.4925
.95	.4999	.5326	.4999
1.00	.5000	.5333	.5000

TABLE 4.—*Values of the F functions*

α	$F_1(\alpha)$	$F_2(\alpha)$	$F_3(\alpha)$
0.00	0.0000	0.0000	0.0000
.05	.0012	.0000	.0012
.10	.0050	.0001	.0047
.15	.0112	.0006	.0106
.20	.0196	.0016	.0176
.25	.0303	.0037	.0261
.30	.0432	.0073	.0351
.35	.0580	.0127	.0449
.40	.0746	.0200	.0556
.45	.0928	.0297	.0692
.50	.1125	.0415	.0807
.55	.1334	.0562	.0995
.60	.1554	.0733	.1096
.65	.1782	.0925	.1267
.70	.2018	.1138	.1457
.75	.2258	.1370	.1661
.80	.2505	.1618	.1881
.85	.2753	.1874	.2118
.90	.3001	.2134	.2357
.95	.3750	.2398	.2608
1.00	.3500	.2666	.2857

In these expressions there appear two types of constants. The constants k_2 and k_3 are of one type and may be referred to as the expansion constants, since these are introduced because of N_2 and N_3. The constants a_0, a_1, and η_s are of the other type and may be referred to as the basic constants, since a_0 relates to the interfacial velocity u_0, a_1, to the local shear and η_s to the thickness of the laminar boundary layer in the upper liquid.

Reasoning in a similar manner, we have for the lower, still liquid,

$$\frac{d^3H'}{d\eta'^3}=\frac{a_1'}{\eta_s'}(-6N_1+32k_2'N_2-30k_3'N_3), \tag{44}$$

$$\frac{d^2H'}{d\eta'^2}=a_1'(J_1+k_2'J_2+k_3'J_3), \tag{45}$$

$$\frac{dH'}{d\eta'}=a_0'+a_1'\eta_s'(G_1+k_2'G_2+k_3'G_3), \tag{46}$$

and

$$H'=a_0'\eta_s'F_0+a_1'\eta_s'^2(F_1+k_2'F_2+k_3'F_3), \tag{47}$$

where N, J, G, and F are the same functions as before but now depend on the independent variable of $\alpha'=\eta'/\eta_s'$. Again, k_2' and k_3' are the expansion constants, and a_0', a_1', and η_s' are the basic constants for the laminar boundary layer in the lower, still liquid.

Equations 43 and 47 are the approximate expressions for the stream functions H and H'. The unknown elements are the basic and expansion constants, which we now proceed to determine.

V. EVALUATION OF THE CONSTANTS

There are a total of six basic constants and four expansion constants in the expressions for H and H', and thus 10 relations are required for their determination. Four such relations are obtained immediately by considering the first of the end conditions in eq 34 and 35 and the continuity conditions, eq 26 and 27. These give, first,

$$a_0+a_1\eta_s A_0=1, \tag{48}$$

where

$$A_0=\frac{1}{2}\left(1+\frac{16}{15}k_2+k_3\right); \tag{49}$$

second,

$$a_0'+a_1'\eta_s' A_0'=0, \tag{50}$$

where

$$A_0'=\frac{1}{2}\left(1+\frac{16}{15}k_2'+k_3'\right); \tag{51}$$

third,

$$a_0=a_0'; \tag{52}$$

and fourth,

$$a_1=-ra_1'M; \tag{53}$$

where

$$M=(1+k_3')/(1+k_3), \quad r^2=(\mu'\rho')/(\mu\rho). \tag{54}$$

The remaining six relations may be obtained from eq 12 and 15 by using one of two methods.

In the first method the left-hand members of eq 12 and 15 are multiplied successively by N_1, N_2, and N_3, and integrated with respect to α or α' between the limits 0 and 1 and set equal to zero, since L is identically equal to zero. That is, putting

$$L=\frac{d^3H}{d\eta^3}+H\frac{d^2H}{d\eta^2}, \tag{55}$$

and

$$L'=\frac{d^3H'}{d\eta'^3}+H'\frac{d^2H'}{d\eta'^2}, \tag{56}$$

the desired six relations are

$$\int_0^1 LN_i\,d\alpha=0,\ (i=1,\ 2,\ 3); \qquad (57, 58, 59)$$

and

$$\int_0^1 L'N_i\,d\alpha'=0,\ (i=1,\ 2,\ 3). \qquad (60, 61, 62)$$

A simpler method would be to use Q_1, Q_2, and Q_3 instead of N_1, N_2, and N_3, where

$$\begin{aligned}
&Q_1=+1, && 0\leqq\alpha \text{ or } \alpha'\leqq 1;\\
&Q_2=+1, && 0\leqq\alpha \text{ or } \alpha'\leqq 1/2;\\
&Q_2=-1, && 1/2\leqq\alpha \text{ or } \alpha'\leqq 1;\\
&Q_3=+1, && 0\leqq\alpha \text{ or } \alpha'\leqq 1/3;\\
&Q_3=-1, && 1/3\leqq\alpha \text{ or } \alpha'\leqq 2/3;\\
&Q_3=+1, && 2/3\leqq\alpha \text{ or } \alpha'\leqq 1.
\end{aligned}$$

The second method, which is the more familiar one, utilizes the following six relations [4]:

$$\int_0^1 Ld\alpha=0; \qquad (63)$$

$$\int_0^1 L'd\alpha=0; \qquad (64)$$

$$\frac{dL}{d\eta}=0,\ \eta=\eta_s; \qquad (65)$$

$$\frac{dL}{d\eta}=0,\quad \eta=0; \qquad (66)$$

$$\frac{dL'}{d\eta'}=0,\quad \eta'=\eta_s'; \qquad (67)$$

$$\frac{dL'}{d\eta'}=0,\quad \eta'=0. \qquad (68)$$

The constants of the present problem have been determined, by using both of the above methods, and the results agreed to the same order of accuracy. The results obtained from eq 63 to 68 will be given here.

From eq 40, 41, and 43, we find from eq 55,

$$\begin{aligned}
L(\eta)=&\frac{a_1}{\eta_s}(-6N_1+32k_2N_2-30k_3N_3)\\
&+a_0a_1\eta_s(J_1F_0+k_2J_2F_0+k_3J_3F_0)\\
&+a_1^2\eta_s^2(J_1F_1+k_2[J_2F_1+F_2J_1]+k_3[J_3F_1+F_3J_1])\\
&+a_1^2\eta_s^2(k_2^2J_2F_2+k_2k_3[J_2F_3+F_2J_3]+k_3^2J_3F_3).
\end{aligned}$$

Substituting in eq 63 and integrating, we find that

$$a_1^2=A_1a_0a_1^2\eta_s^2+A_2a_1^3\eta_s^2, \qquad (69)$$

where

$$A_1=(a_{01}+a_{02}k_2+a_{03}k_3)/(1+k_3), \qquad (70)$$

and

$$A_2=(a_{11}+a_{12}k_2+a_{13}k_3+a_{22}k_2^2+a_{23}k_2k_3+a_{33}k_3^2)/(1+k_3). \qquad (71)$$

The values of the coefficients with the double subscripts occurring in eq 70 and 71 are

$$a_{01}=0.15000, \quad a_{11}=0.029365, \quad a_{22}=0.0308,$$
$$a_{02}=0.26667, \quad a_{12}=0.07619, \quad a_{23}=0.0758,$$
$$a_{03}=0.21425, \quad a_{13}=0.07625, \quad a_{33}=0.0400.$$

By treating eq 64 in a similar manner, we find that

$$a_1'^2=A_1'a_0'a_1'^2\eta_s'^2+A_2'a_1'^3\eta_s'^3, \tag{72}$$

where

$$A_1'=(a_{01}+a_{02}k_2'+a_{03}k_3')/(1+k_3'), \tag{73}$$

and

$$A_2'=(a_{11}+a_{12}k_2'+a_{13}k_3'+a_{22}k_2'^2+a_{23}k_2'k_3'+a_{33}k_3'^2)/(1+k_3'). \tag{74}$$

Since from eq 55

$$\frac{dL}{d\eta}=\frac{d^4H}{d\eta^4}+\frac{dH}{d\eta}\frac{d^2H}{d\eta^2}+H\frac{d^3H}{d\eta^3},$$

and

$$\frac{dN_1}{d\alpha}=1, \quad \frac{dN_2}{d\alpha}=1, \quad \frac{dN_3}{d\alpha}=2, \quad \eta=0, \quad \alpha=0,$$
$$\frac{dN_1}{d\alpha}=-1, \quad \frac{dN_2}{d\alpha}=1, \quad \frac{dN_3}{d\alpha}=-2, \quad \eta=\eta_s, \quad \alpha=1,$$

we find from eq 65

$$\frac{a_1}{\eta_s}(6+32k_2+60k_3)=0, \tag{75}$$

and from eq 66

$$\frac{a_1}{\eta_s^2}(-6+32k_2-60k_3)=-a_0a_1(1+k_3). \tag{76}$$

Adding eq 75 to eq 76, we have

$$64k_2=-a_0\eta_s^2(1+k_3). \tag{77}$$

Since η_s is finite and a_1 does not vanish, we have, from eq 75,

$$60k_3=-6-32k_2. \tag{78}$$

We have from eq 77, using eq 48, the relation

$$64k_2=-\frac{4a_0(1-a_0)^2}{a_1^2}\left[(1+k_3)/\left(1+\frac{16}{15}k_2+k_3\right)^2\right], \tag{79}$$

where η_s does not appear. It may be emphasized that eq 78 and 79 are two relations expressing the expansion constants k_2 and k_3 in terms of the basic constants a_0 and a_1.

In a similar manner we obtain from eq 67 and 68 the two relations

$$60k_3' = -6 - 32k_2', \tag{80}$$

$$64k_2' = -\frac{4a_0'^3}{a_1'^2}\left[(1+k_3')/\left(1+\frac{16}{15}k_2'+k_3'\right)^2\right]. \tag{81}$$

Equations 48, 50, 52, 53, 69, 72, 78, 79, 80, and 81 are the desired 10 relations for determining the 10 constants appearing in the expressions for H and H' given by eq 43 and 47, respectively. In principle the determination of the constants in a direct manner is possible, but since this is tedious, it may be carried out by successive approximations. The successive approximations to the values of the constants give the successive approximations to the present boundary-layer problem.

VI. FIRST APPROXIMATE SOLUTION FOR THE LAMINAR BOUNDARY LAYERS

In the first approximate solution it is assumed that the expansion constants k_2, k_3, k_2', and k_3' are zero.

Consider the relations

$$a_0 + a_1\eta_s A_0 = 1, \tag{48a}$$

$$a_0' + a_1'\eta_s' A_0' = 0, \tag{50a}$$

$$a_0 = a_0', \tag{52a}$$

$$a_1 = -ra_1'M, \quad [r^2 = (\mu'\rho')/(\mu\rho)], \tag{53a}$$

$$a_1^2 = A_1 a_0 a_1^2 \eta_s^2 + A_2 a_1^3 \eta_s^3, \tag{69a}$$

and

$$a_1'^2 = A_1' a_0' a_1'^2 \eta_s'^2 + A_2' a_1'^3 \eta_s'^3. \tag{72a}$$

Here the constants A_0, A_0', M, A_1, A_1', A_2 and A_2' are functions of k_2, k_3, k_2', and k_3' and may be determined from eq 49, 51, 54, 70, 71, 73, and 74. For k_2, k_3, k_2', and k_3' all equal to zero, we obtain

$$A_0 = A_0' = 0.50000,$$
$$A_1 = A_1' = 0.15000,$$
$$A_2 = A_2' = 0.023936,$$
$$M = 1.$$

Now, the determination of the unknown quantities a_0, a_1, η_s and a_0', a_1', η_s' from the above six relations, 47a to 72a, is an easy task once a specific value is assigned to r. Separate determinations were made by selecting nine values for r, namely, $r^2 = 0.00$, 0.01, 0.10, 0.3162, 1, 3.162, 10.0, 100, and ∞. The results are shown in table 5.

TABLE 5.—*First approximate values of the constants* a_0, a_1, a_1', η_s *and* η_s'

$r^2=(\mu'\rho')/(\mu\rho)$

r^2	a_1	a_1', a_0	or a_0'	η_s	η_s'	H_s	H_s'
0.00	------	0.6038	1.000	------	3.309	------	0.995
.01	0.0540	.5402	0.9285	2.611	3.433	2.552	.959
.10	.1388	.4390	.8085	2.744	3.678	2.582	.893
.3162	.2031	.3614	.7100	2.845	3.923	2.595	.838
1.0	.2727	.2724	.5910	2.995	4.331	2.616	.772
3.162	.3397	.1911	.4646	3.146	4.851	2.630	.679
10	.3916	.1238	.3479	3.324	5.605	2.672	.590
100	.4494	.0449	.1773	3.655	7.844	2.750	.423
∞	.4839	------	.000	4.124	------	2.884	------

The expressions for H and H' from eq 43 and 47, respectively, wherein the constants k and k' are put equal to zero and the values of the basic constants are taken from table 5, constitute the first approximate solution of the laminar boundary layers at the interface of two liquids, one of which is still and the other moving. More specifically, in the upper liquid

$$H=a_0\eta_s F_0(\eta/\eta_s)+a_1{}^2\eta_s F_1(\eta/\eta_s),\quad \frac{dH}{d\eta}=a_0+a_1\eta_s G_1(\eta/\eta_s),$$

and in the lower liquid

$$H'=a_0'\eta_s' F_0(\eta'/\eta_s')+a_1'^2\eta_s'^2 F_1(\eta'/\eta_s'),\quad \frac{dH'}{d\eta'}=a_0'+a_1'\eta_s' G_1(\eta'/\eta_s').$$

The numerical values of F_0, F_1, and G_1 are given in tables 3 and 4.

It may be of interest to note that the case $r^2=\infty$ can be physically interpreted as representing the case in which the lower liquid has an infinite viscosity, which is obviously the case for a liquid flowing over a plate. The solution obtained here for $r^2=\infty$ is identical with Pohlhausen's fourth approximation. In the present analysis this constitutes only the first approximate solution.

VII. SECOND APPROXIMATE SOLUTION OF THE LAMINAR BOUNDARY LAYERS

Inserting the first approximate values of a_0, a_1, and a_0', a_1' from table 5 in eq 78, 79, 80, and 81, we obtain a set of values for k_2, k_3, k_2', and k_3', after discarding the squares and the higher powers of these constants. The results are given in table 6 for the various values of r^2.

TABLE 6.—*Second approximate values of the expansion constants* k_2, k_3, k_2', *and* k_3'

$r^2=(\mu'\rho')/(\mu\rho)$

r^2	k_2	k_3	k_2'	k_3'	M
0.00	------	------	−0.2600	+0.0382	------
.01	−0.1354	−0.0278	−.2600	+.0382	1.0681
.10	−.1259	−.0328	−.2600	+.0382	1.0737
.3162	−.1162	−.0380	−.2600	+.0382	1.0816
1.0	−.1037	−.0446	−.2600	+.0382	1.0869
3.162	−.0897	−.0522	−.2600	+.0382	1.0956
10	−.0734	−.0608	−.2600	+.0382	1.1057
100	−.0429	−.0771	−.2600	+.0382	1.1252
∞	.0000	−.1000	--------	--------	--------

With these, corresponding values of the coefficients A_0, A', A_1, A_1', A_2, A_2', and M are computed. The results are shown in table 7. With the values of the coefficients thus known, the second approximate values of the basic constants are determined by the same equations as for the first approximate solution, that is, eq 48a to 72a, inclusive. The results of this determination are given in table 8.

Expressions for H and H' from eq 43 and 47, respectively, where the expansion constants are given in table 6 and the basic constants are given in table 8, constitute the second approximate solution of the laminar layers boundary problem for the interface between two liquids.

TABLE 7.—*Second approximate values of the auxiliary constants* A_0, A_1, A_2, A_0', A_1', *and* A_2'

$r^2=(\mu'\rho')/(\mu\rho)$

r^2	A_0	A_1	A_2	A_0'	A_1'	A_2'
0.00	-------	-------	-------	0.3806	0.08562	0.01336
.01	0.4139	0.1110	0.01830	.3806	.08562	.01336
.10	.4164	.1131	.01871	.3806	.08562	.01336
.3162	.4190	.1155	.01917	.3806	.08562	.01336
1.00	.4224	.1181	.01970	.3806	.08562	.01336
3.162	.4260	.1212	.02038	.3806	.08562	.01336
10	.4304	.1250	.02107	.3806	.08562	.01336
100	.4382	.1321	.02245	.3806	.08562	.01336
∞	.4600	.1427	.02460	------	--------	--------

TABLE 8.—*Second approximate values of the basic constants* a_0, a_1, a_1', η_s, *and* η_0

$r^2=(\mu'\rho')/(\mu\rho)$

r^2	a_1	a_1'	a_0 or a_0'	η_s	η_s'	H_s	H_s'
0.00	-------	−0.5906	1.0000	-------	4.449	3.012	1.041
.01	0.0567	−.5329	0.9282	3.069	4.576	3.004	0.993
.10	.1456	−.4287	.8082	3.163	4.953	2.991	.936
.3162	.2144	−.3527	.7088	3.241	5.280	2.990	.875
1.0	.2899	−.2668	.5888	3.358	5.793	2.991	.798
3.162	.3611	−.1854	.4619	3.498	6.545	2.996	.707
10	.4174	−.1194	.3446	3.648	7.582	3.016	.602
100	.4817	−.0428	.1739	3.913	10.672	3.055	.434
∞	.5196	-------	.0000	4.277	------	------	------

VIII. QUALITY OF THE APPROXIMATIONS

The quality of the approximations may be studied conveniently by substituting the approximate expressions for H and H' and for their derivatives into the differential equations, eq 12 and 15, and then considering the magnitude of the remainders. Let the remainders be denoted by ΔL and $\Delta L'$:

$$\Delta L=\frac{d^3H}{d\eta^3}+H\frac{d^2H}{d\eta^2},$$

and

$$\Delta L'=\frac{d^3H'}{d\eta'^3}+H'\frac{d^2H'}{d\eta'^2}.$$

If the ratios

$$\Delta L/(d^3H/d\eta^3)_{\max} \text{ and } \Delta L'/(d^3H'/d\eta'^3)_{\max}$$

become smaller in the successive approximations, the magnitude of decrease is a measure of the improvements in the approximations.

We have computed these remainders only for the two extreme

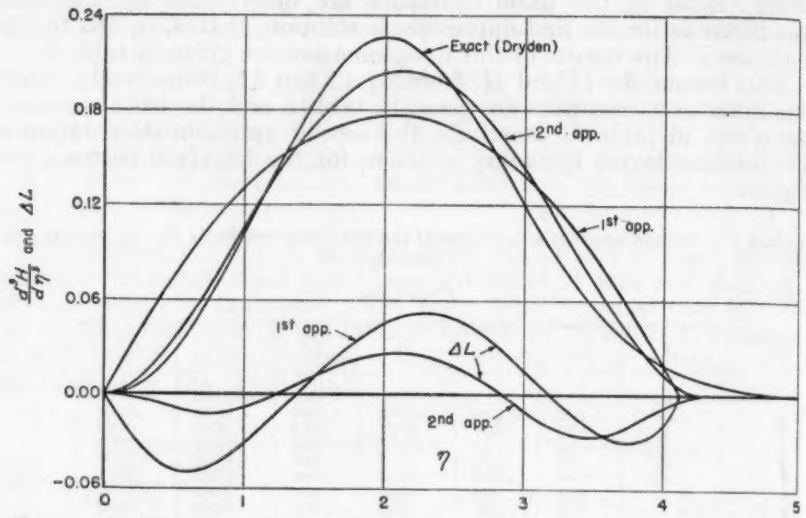

FIGURE 2—*Remainders of the first and of the second approximations for the case* $r^2=\infty$.

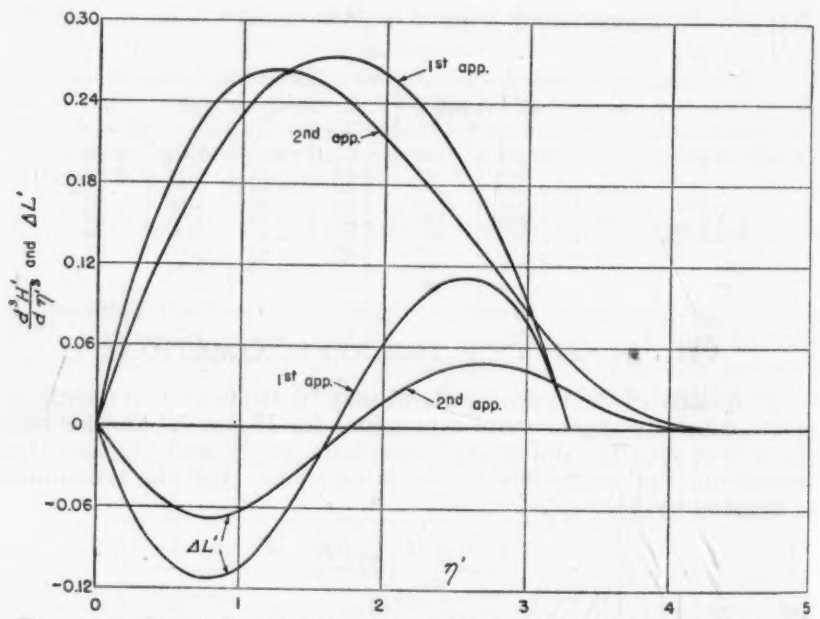

FIGURE 3—*Remainders of the first and of the second approximations for the case* $r^2=0$.

cases represented by $r^2=\infty$ and $r^2=0$. The values of the remainders together with the values of the third derivatives of H and H', are given in figures 2 and 3, respectively. The case of a liquid of finite

viscosity moving over a liquid of infinite viscosity is represented by $r^2=\infty$. As mentioned before, this is mathematically identical with the Blasius problem of flow over a plate. In examining the curves in figure 2, we see that the amplitude of the oscillation of the remainder in the second approximate solution is only about half as large as in the first approximation, indicating that the improvement in the second approximate solution is appreciable. In the second approximate solution, the maximum value of the remainder is 0.027; the maximum value of the third derivative, 0.25. It is thus seen that the remainders are relatively small. In this same figure we give also the curve of the third derivative of H from the exact solution by Dryden [5]. The agreement between the second approximate solution and the exact solution is rather close. The velocity gradient at $y=0$, from the second approximate solution, is

$$\frac{1}{U}\frac{\partial u}{\partial y}=0.3307\sqrt{U/(\nu x)}.$$

In the exact solution the corresponding coefficient has the value 0.3320, thus indicating that the error in the value of this quantity from the second approximate solution is only 0.39 percent.

A liquid of infinite viscosity moving over a liquid of finite viscosity is represented by $r^2=0$. Physically, it would seem that this is the case of a solid surface moving in a still liquid. The curves in figure 3 also show that in this case the remainder of the second approximate solution has been reduced and has become about half as large as the corresponding quantity in the first approximate solution. But the accuracy obtained is not as satisfactory as in the case $r^2=\infty$, since the remainders are relatively larger. Apparently to obtain the same degree of accuracy as was obtained in the case $r^2=\infty$, and with the second approximation it will be necessary to introduce the expansion functions k_4N_4 and k_5N_5.

IX. PHYSICALLY SIGNIFICANT QUANTITIES OF THE LAYERS

Among the quantities of the laminar layers at the interface of the two liquids, one at rest and the other moving over it, the following are of practical significance: (1) The intensity of the viscous stresses at the surface of separation, (2) the thickness of the layers, and (3) the distribution of the velocities in the layers. The computation of these quantities will be made, using the second approximate solution of the analysis.

1. LOCAL STRESS AT THE SURFACE OF SEPARATION

The stress in question is determined from the velocity gradient of the upper liquid at the surface of separation:

$$\tau=\mu\left(\frac{\partial u}{\partial y}\right)_{y=0}.$$

From eq 19

$$\tau=\mu\,\frac{U}{\delta}\left(\frac{d^2H}{d\eta^2}\right)_0,$$

or

$$\tau=\frac{2\nu}{\delta U}\left(\frac{d^2H}{d\eta^2}\right)_0\frac{\rho}{2}U^2.$$

Substituting from eq 14,

$$\tau=\sqrt{2}\left(\frac{d^2H}{d\eta^2}\right)_0\left(\frac{Ux}{\nu}\right)^{-\frac{1}{2}}\frac{\rho}{2}U^2.$$

If we use the velocity gradient of the lower liquid, we obtain in the same manner,

$$\tau=-\sqrt{2}\left(\frac{d^2H'}{d\eta'^2}\right)_0\left(\frac{Ux}{\nu'}\right)^{-\frac{1}{2}}\frac{\rho'}{2}U^2.$$

Putting

$$\sqrt{2}\left(\frac{d^2H}{d\eta^2}\right)_0=\sqrt{2}a_1(1+k_3)=s,$$

and

$$-\sqrt{2}\left(\frac{d^2H'}{d\eta'^2}\right)_0=-\sqrt{2}a_1'(1+k_3')=s',$$

we have the local stresses

$$\tau=s\left(\frac{Ux}{\nu}\right)^{-\frac{1}{2}}\frac{\rho}{2}U^2, \tag{82}$$

or

$$\tau=s'\left(\frac{Ux}{\nu'}\right)^{-\frac{1}{2}}\frac{\rho'}{2}U^2. \tag{83}$$

The computed values of s and s' as functions of r^2 are given in table 9.

TABLE 9.—*Values of the constants s and s′ in the expressions of the local stress at the interface, eq 82 and 83*

$r^2=(\mu'\rho')/(\mu\rho)$

r^2	s	s'
0.00	----------	0.8672
.01	0.0782	.7825
.10	.1992	.6295
.3162	.2917	.5178
1.0	.3917	.3918
3.162	.4840	.2722
10	.5543	.1753
100	.6287	.0628
∞	.6612	----------

2. THICKNESSES OF THE LAYERS

Since the velocities in the laminar boundary layers approach the limiting values in an asymptotic manner, the definition of the thickness of the layers becomes a matter of convention. Of particular utility are the following definitions. See figure 4.

$$2\int_0^{y_1}(U-u)dy=(U-u_0)\delta_1, \tag{84}$$

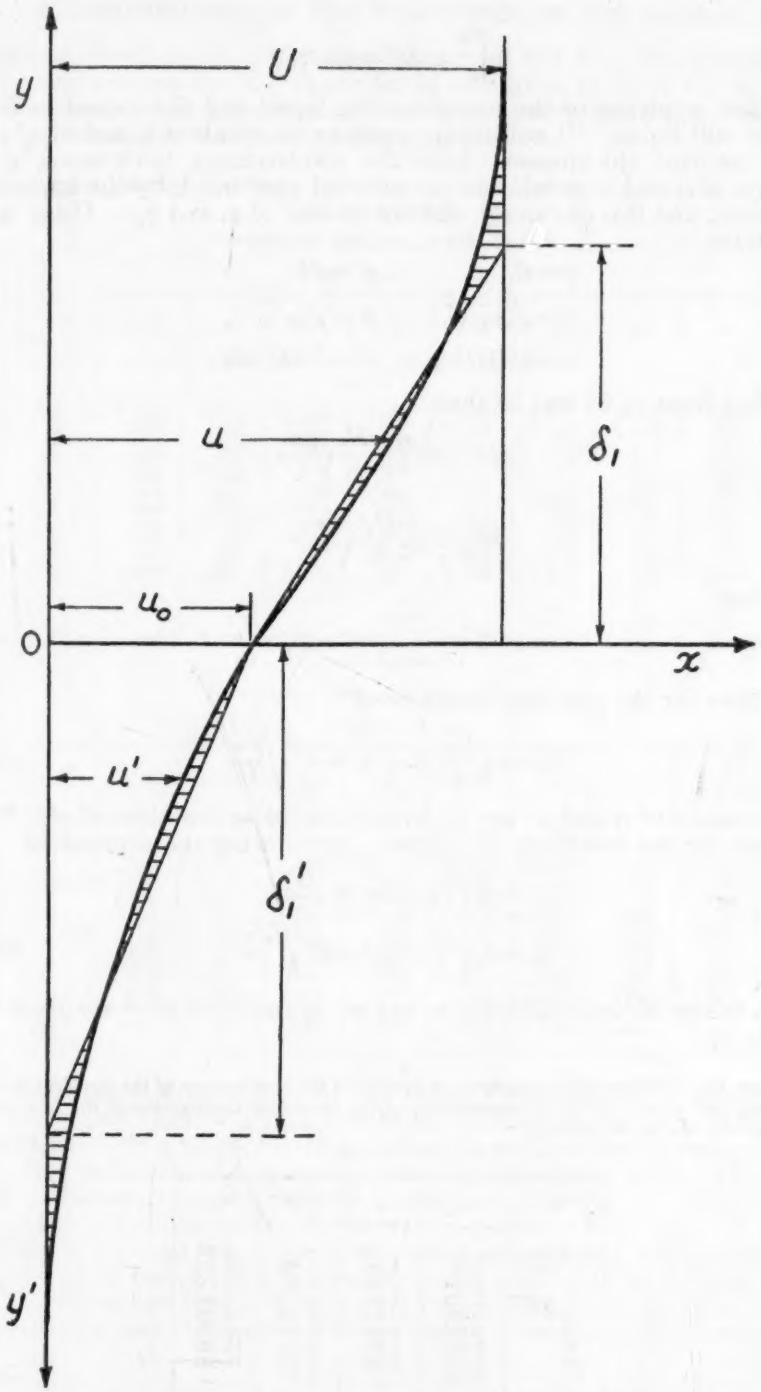

FIGURE 4.—*The gradient thicknesses of the interfacial laminar boundary layers.*

and

$$2\int_0^{y_s'} u'dy' = u_0\delta_1', \tag{85}$$

the first applying to the upper moving liquid and the second to the lower still liquid. It will be appropriate to speak of δ_1 and of δ_1' as the gradient thicknesses. Like the displacement thicknesses, the values of δ_1 and δ_1' would not be affected very much by the approximations, and this obviously, can not be said of y_s and y_s'. Using the relations

$$y=\eta\delta, \qquad y'=\eta'\delta',$$
$$\delta=\sqrt{2\nu x/U}, \qquad \delta'=\sqrt{2\nu' x/U},$$
$$u=UdH/d\eta, \qquad u'=UdH'/d\eta',$$

we find from eq 84 and 85 that

$$\delta_1=2\sqrt{2}\frac{\eta_s-H_s}{1-a_0}\sqrt{\frac{\nu x}{U}},$$

and

$$\delta_1'=2\sqrt{2}\frac{H_s'}{a_0}\sqrt{\frac{\nu' x}{U}}.$$

Putting

$$n=2\sqrt{2}\frac{\eta_s-H_s}{1-a_0}, \quad n'=2\sqrt{2}\frac{H_s'}{a_0},$$

we have for the gradient thicknesses,

$$\delta_1=n\sqrt{\frac{\nu x}{U}}, \text{ and } \delta_1'=n'\sqrt{\frac{\nu' x}{U}}. \tag{86}$$

The values of n and n' are given in table 10 as functions of r^2. We obtain for the boundary thicknesses, introducing the expressions

$$m=\sqrt{2}\eta_s, \quad m'=\sqrt{2}\eta_s':$$

$$y_s=m\sqrt{\frac{\nu x}{U}}, \quad y_s'=m'\sqrt{\frac{\nu' x}{U}}. \tag{87}$$

The values of the coefficients m and m' as functions of r^2 are given in table 10.

TABLE 10.—*Values of the constants n and n' in the expressions of the gradient thickness and m and m' in the expressions of the boundary thicknesses of the two laminar layers, eq 86 and 87*

$r^2=(\mu'\rho')/(\mu\rho)$

r^2	n	n'	m	m'
0.00	.....	2.943	.....	6.291
.01	2.270	3.026	4.339	6.470
.10	2.344	3.304	4.472	7.003
.3162	2.428	3.493	4.582	7.466
1.0	2.531	3.831	4.748	8.191
3.162	2.664	4.328	4.946	9.255
10	2.813	4.940	5.158	10.721
100	3.071	7.063	5.533	15.090
∞	3.455	-------	6.047	-------

3. DISTRIBUTION OF THE VELOCITIES IN THE LAYERS

These velocities are determined from eq 42 and 46. The results of the computations for the upper liquid are given in table 11, where u/D is tabulated as a function of y/y_s for various values of r^2. Similar results for the lower liquid are given in table 12.

TABLE 11.—*Velocity distribution in the interfacial laminar layer of the upper, moving liquid*

The boundary thickness y_s is given by eq 87

$r^2=(\mu'\rho')/(\mu\rho)$

y/y_s \ r^2	0.010	0.100	0.316	1.000	3.16	10	100	∞
	u/U							
0.0	0.9282	0.8082	0.7088	0.5888	0.4619	0.3446	0.1739	0.0000
.1	.9449	.8521	.7747	.6807	.5808	.4862	.3466	.1994
.2	.9602	.8929	.8363	.7667	.6917	.6204	.5122	.3935
.3	.9735	.9279	.8892	.8412	.7891	.7387	.6609	.5723
.4	.9838	.9557	.9316	.9015	.8685	.8359	.7850	.7271
.5	.9913	.9758	.9626	.9457	.9273	.9089	.8797	.8440
.6	.9961	.9889	.9826	.9747	.9660	.9573	.9432	.9252
.7	.9988	.9962	.9933	.9910	.9878	.9848	.9801	.9727
.8	.9998	.9991	.9985	.9980	.9973	.9966	.9960	.9938
.9	.9999	.9999	.9998	.9998	.9997	.9996	.9996	.9995
1.0	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000

TABLE 12.—*Velocity distribution in the interfacial laminar layer of the lower, still liquid*

The boundary thickness y_s' is given by eq 87

$r^2=(\mu'\rho')/(\mu\rho)$

y'/y_s' \ r^2	0.00	0.010	0.100	0.316	1.000	3.16	10	100
	u'/U							
0.0	1.0000	0.9282	0.8082	0.7088	0.5888	0.4619	0.3446	0.1739
.1	.7337	.6811	.5930	.5200	.4320	.3389	.2527	.1276
.2	.4980	.4624	.4023	.3530	.2932	.2301	.1716	.0866
.3	.3121	.2897	.2524	.2213	.1838	.1441	.1075	.0542
.4	.1765	.1639	.1427	.1250	.1039	.0814	.0608	.0306
.5	.0886	.0822	.0717	.0628	.0522	.0404	.0305	.0154
.6	.0369	.0343	.0298	.0262	.0217	.0171	.0131	.0064
.7	.0119	.0112	.0098	.0092	.0070	.0055	.0041	.0020
.8	.0026	.0025	.0022	.0021	.0016	.0011	.0009	.0004
.9	.0007	.0006	.0005	.0004	.0003	.0002	.0001	.0001
1.0	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000

A more suggestive picture of the velocity distribution is obtained by plotting u/U against y/y_s, y now being the distance from the surface of separation to a point, above or below the surface, and y_s being the boundary thickness of the layer situated in the upper liquid. Figure 5 gives the velocities for identical liquids, $\mu=\mu'$ and $\rho=\rho'$. Figure 6 gives the velocities for $\nu'=7.85\nu$ and $\rho'=1.14\rho$. This case will be realized if we take water for the upper moving liquid and aqueous solution of 56 percent glycerol for the lower, still liquid, both being at 20° C. These two figures demonstrate the very large influence that the increased viscosity of the lower liquid has on the velocity distribution.

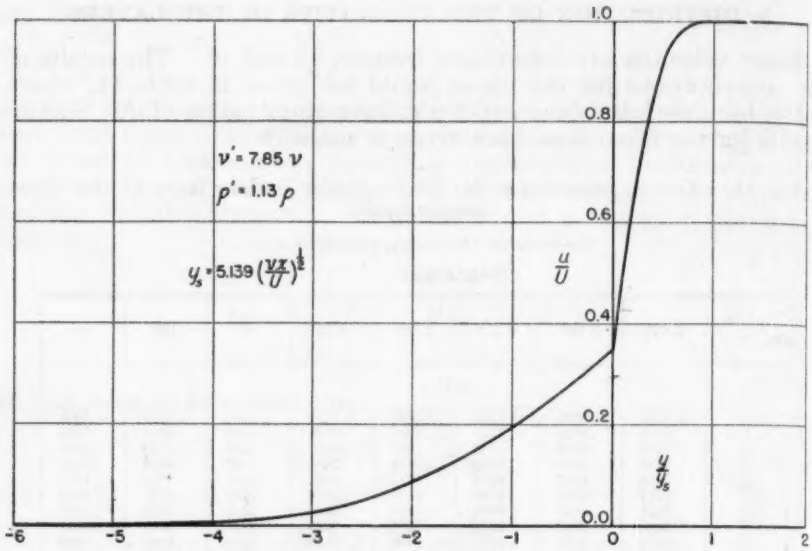

FIGURE 5.—*Interfacial laminar velocity distribution for the case* $r^2 = 1$.

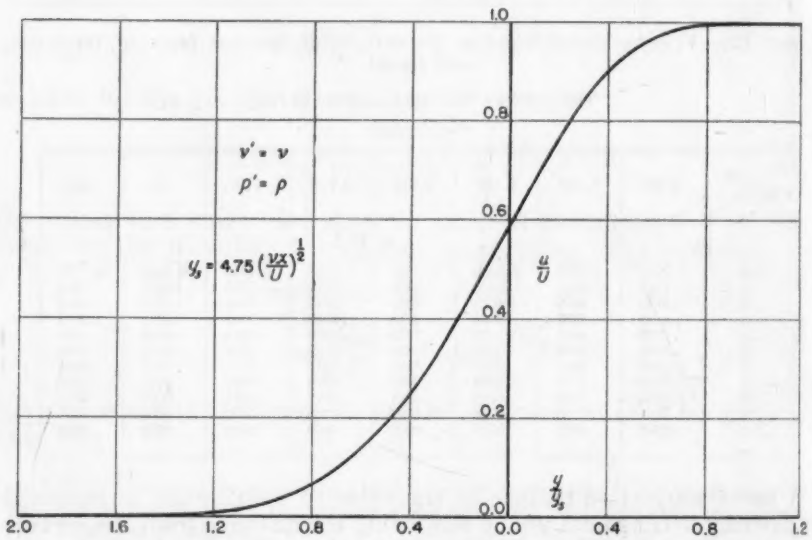

FIGURE 6.—*Interfacial laminar velocity distribution for the case* $r^2 = 10$.

X. TRANSVERSAL VELOCITIES OF THE LAYERS

The expressions of the transversal velocities, v and v', in terms of H and η, may be derived conveniently from the condition of continuity eq 4. Since at the interface, v and v' vanish, we have

$$v = -\int_0^y \frac{\partial u}{\partial x}\, dy.$$

This yields, using eq 13, 14, and 18, the relation

$$\frac{\delta v}{\nu}=\int_0^{\eta}\frac{d^2H}{d\eta^2}\eta d\eta.$$

Integrating by parts and noting that $H=0$ when $\eta=0$, we obtain

$$\frac{\delta v}{\nu}=\frac{dH}{d\eta}\eta-H, \tag{88}$$

which is the expression for the transversal velocities at the point (η, δ).

The corresponding expression for the lower fluid is

$$\frac{\delta' v'}{\nu'}=\frac{dH'}{d\eta'}\eta'-H'. \tag{89}$$

Thus, at the points of the lower liquid and in the region outside of the layer, $\eta'>\eta_s'$, there is a weak current moving normally upward toward the interface. The strength of the current is given by

$$v'=-\frac{\nu' H_s'}{\delta'}. \tag{90}$$

In a sense, the boundary layer of the upper liquid acts as a pump, raising the small portions of the lower liquid to the level of the interface, then causing these portions to move horizontally. So long as these motions as required by the theory are not interfered with, the steadiness of the layer will be assured.

The author acknowledges gratefully the editorial assistance in the preparation of this paper furnished by George W. Patterson, and also the valuable suggestions offered by Galen B. Schubauer.

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(Reprinted from J. Math. Phys., December 1942.) 20 pages, with cover, 25 cents.

MT20. Table of integrals $\int_0^x J_0(t)dt$ and $\int_0^x Y_0(t)dt$:

Values of the two integrals are given for $x=0(.01)10$ to 10 decimal places. (Reprinted from J. Math. and Phys., May 1943.) 12 pages, with cover, 25 cents.

MT21. Table of $Ji_0(x)=\int_x^\infty \frac{J_0(t)}{t}dt$ and Related Functions:

Table I: $Ji_0(x)$ to 10 decimal places and $F(x)=Ji_0(x)+\log_e 1/2x$ to 12 decimal places for $x=0(.1)3$ with even central differences of $F(x)$.
Table II: $Ji_0(x)$ to 10 decimal places, for $x=3(.1)10(1)22$ with even central differences up to $x=100$.
Table III: "Reduced" derivatives of $F(x)$ for $x=10(1)21$ and $n=0(1)13$, to 12 decimal places.
(Reprinted from J. Math. Phys., June 1943.) 7 pages, with cover, 25 cents.

MT22. Table of Coefficients in Numerical Integration Formulae:
The values of $B^{(n)}{}_n(1)/n!$ and $B^{(n)}{}_n/n!$ where $B^{(n)}{}_n(1)$ denotes the n^{th} Bernoulli polynomial of the nth order for $x=1$ and $B^{(n)}{}_n$ denotes the n^{th} Bernoulli number of the n^{th} order, were computed for $n=1, 2, \ldots 20$. The quantities $B^{(n)}{}_n(1)/n!$ are required in the Laplace formula of numerical integration employing forward differences, as well as in the Gregory formula. The quantities $B^{(n)}{}_n/n!$ are used in the Laplace formula employing backward differences.
(Reprinted from J. Math. Phys., June 1943.) 2 pages, with cover, 25 cents.

MT23. TABLE OF FOURIER COEFFICIENTS.
Whenever $\varphi(x)$ is a known polynomial whose degree does not exceed 10, the present table of the functions
$S(k,n)=\int_0^1 x^k \sin n\pi x\,dx$ and $C(k,n=\int_0^1 x^k \cos n\pi x\,dx$ to 10D$(1\leqslant k\leqslant 10, 1\leqslant n\leqslant 100)$, will facilitate the evaluation of the first hundred Fourier Coefficients.
Reprinted from J. Math. Phys. Sept., 1943.) 11 pages, with cover, 25 cents.

MT24. COEFFICIENTS FOR NUMERICAL DIFFERENTIATION WITH CENTRAL DIFFERENCES.
Coefficients are given for derivatives as far as the 52d. For the first 30 derivatives, exact values are given for coefficients of the first 30 differences, and also exact values are given for some coefficients of differences beyond the 30th. For the other coefficients, values are given to 18 significant figures.
(Reprinted from J. Math. Phys., Sept. 1943) 21 pages, with cover, 25 cents.

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A mailing list is maintained for those who desire to receive announcements regarding new tables as they become available.